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Effects of intense ageing on volatility and chemical composition of urban aerosol particles

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Introduction

Aerosol particles form a ubiquitous component of the Earth’s atmosphere, which has profound effect on for example visibility, human health and climate change.

A significant source of organic aerosol (OA) is oxidation of volatile organic compounds (VOC) in the gas phase, leading to formation of less volatile compounds. These can nucleate to form secondary organic aerosol (SOA) particles or condense on existing particles. The lifetimes and fates of atmospheric species depend strongly on physical properties, e.g. phase, and chemical properties.

We here characterize particles at street level in central Copenhagen in terms of mass and number, chemical composition and volatility. Particles were in some cases exposed to additional ageing.

Methods

Particles were sampled in central Copenhagen during Jan-Feb 2012 and characterized using a scanning mobility particle sizer (SMPS), an aerosol mass spectrometer (AMS) and a thermodenuder (TD). Effects of ageing were investigated with a potential aerosol mass (PAM) chamber.

PAM is defined as the maximum aerosol mass produced through oxidation of precursor gasses. In the PAM chamber, SOA production occurs in a highly oxidizing environment ensuring rapid reaction of precursor gasses. Thus, all processes instigated by photo-oxidation of gas phase components occur in minutes in PAM as they would over hours or days in the atmosphere (Kang et al., 2007).

In the present study, particles were exposed to high levels of ozone (up to 16 ppm) and OH radical (exposure up to 1-2·10¹² molecules·s·cm⁻³, corresponding to 1-2 weeks of OH exposure under ambient conditions).

Results

Large numbers of fresh particles were generated by nucleation in the PAM chamber, but these were too small to significantly alter the particle mass detected with AMS. However, alterations of the organic fraction were detectable with AMS, possibly a consequence of condensation or heterogeneous reactions. The main change was an increase of O:C ratio and decrease in H:C ratio (Figure 1).

Also, volatilities of the OA components were influenced by the reaction in the PAM chamber (see Figure 2): The fractions of m/z 43 and 44 to total OA mass (f₄₃ and f₄₄) were used as markers for hydrocarbon like and oxidized OA, respectively. Absolute values of f₄₃ and f₄₄ of particles exposed to elevated temperatures in the TD varied, depending on whether particles were sampled through the PAM chamber.

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