Improving the representation of biomass burning emissions and their aging in the VBS-CAMx based on novel smog chamber experiments conducted at wintertime temperatures

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Organic gases undergoing conversion to form secondary organic aerosol (SOA) during atmospheric aging are largely unidentified, particularly in regions influenced by anthropogenic emissions. SOA dominates the atmospheric organic aerosol (OA) burden and this knowledge gap contributes to uncertainties in aerosol effects on climate and human health. Residential wood combustion may be an important source of primary organic aerosol (POA) emissions and potentially SOA precursors, particularly in regions with cooler climates. Previous work shows that traditional SOA precursors account for less than 20% of the observed SOA formed from residential wood combustion emissions (Grieshop et al., 2009). A significant fraction of SOA is postulated to derive from non-traditional intermediate and semi-volatile organic compounds, which are not currently included in emission inventories.

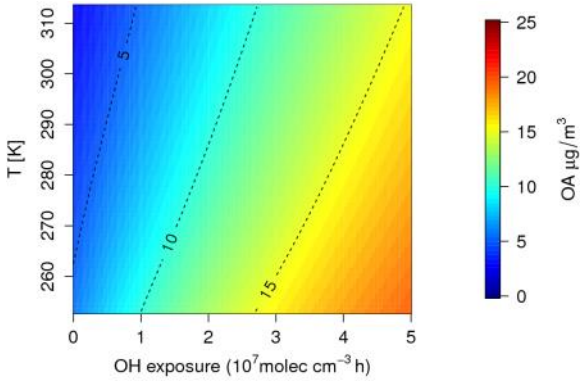
In this study, novel wood combustion aging experiments performed at different temperatures (263.15 K and 288.15 K) in a ~7 m^3 smog chamber (Bruns et al., in prep.) were modelled using a two-dimensional volatility basis set (VBS) box model, representing the emission partitioning and their oxidation by OH. We combine unprecedented measurements of non-traditional volatile organic compounds (NTVOCs) measured by a high-resolution proton transfer reaction mass spectrometer and organic aerosol measurements from an aerosol mass spectrometer to constrain the volatility distribution of the primary biomass burning emissions.

More than 30000 box model simulations were performed to follow the evolution of oxidation products of the semi-volatile and volatile precursors with aging and to retrieve the combination of parameters that fit best the observed organic aerosol mass and O:C ratios. These parameters include the NTVOCs reaction rates and yields as well as enthalpies of evaporation and the O:C of secondary organic aerosol surrogates. The latter was also constrained by the molecular identity of the contributing precursor gases.

We show that the molar abundance of SOA precursors is, on average, five times higher than that of semi-volatile compounds. The mass yields of these precursors determined for a wide range of atmospherically relevant temperatures and organic aerosol (OA) concentrations were predicted to vary between 8 and 30 % after 5 hours of aging (Figure 1). We assessed for the first time the temperature dependence of SOA yields and determined the enthalpy of evaporation of SOA compounds ranging between 55000 J mol^{-1} and 35000 J mol^{-1}, which implies a yield increase of c.a. 0.03 - 0.06 % K^{-1} with decreasing temperature.

The improved scheme was implemented in CAMx (Comprehensive Air Quality Model with extensions) to predict the burden and oxidation state of primary and secondary biomass burning aerosols in ambient air. The evaluation of this model for one of the EMEP intensive campaigns in a winter episode (February-March 2009) against aerosol mass spectrometers (AMS) measurements performed at 11 sites in the Europe will be discussed.

Figure 1: variation of biomass burning OA concentration with aging at different temperatures. Initial OA concentration = 60 µg m^{-3}.



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Bruns, E. A. et al., in prep.

Grieshop, A. P., et al., Atmos Chem Phys 9, 1263-1277 (2009).