

ENVIRONMENT/ECOLOGY

Special Topic: Air Pollution and Control

Modelling secondary organic aerosols in ChinaQi Chen^{1,*}, Tzung-May Fu^{2,*}, Jianlin Hu^{3,*}, Qi Ying⁴ and Lin Zhang²

Secondary organic aerosols (SOA) are important components of atmospheric particulate matter, which affect radiative balance and cloud properties, and are harmful to human health. More than half of the tropospheric organic aerosol (OA) mass is secondary [1]. However, representing the sources and the atmospheric evolution of SOA in models is difficult because of their chemical complexity and process nonlinearity (Fig. 1). Coal combustion, traffic,

cooking, biomass burning and biogenic emissions, for example, contribute large quantities of primary OA and secondary precursors, which may form SOA via atmospheric oxidation and condensation of low-volatility products. Once formed, the amounts and properties of SOA continue to be altered by oxidative ageing, condensation, evaporation, and heterogeneous and aqueous chemistry. Meteorological conditions (e.g. temperature and humidity), as well as particle-phase

water and other inorganic components, also play important roles in SOA formation [2]. In China, SOA constitutes 15–30% of the surface mass of PM_{2.5} (particulate matter with an aerodynamic diameter less than 2.5 μm) during haze events, and significant variations in the relative abundance and the characteristics of SOA have been observed [3]. However, air quality models have difficulties in reproducing the mass concentrations and variability of OA,

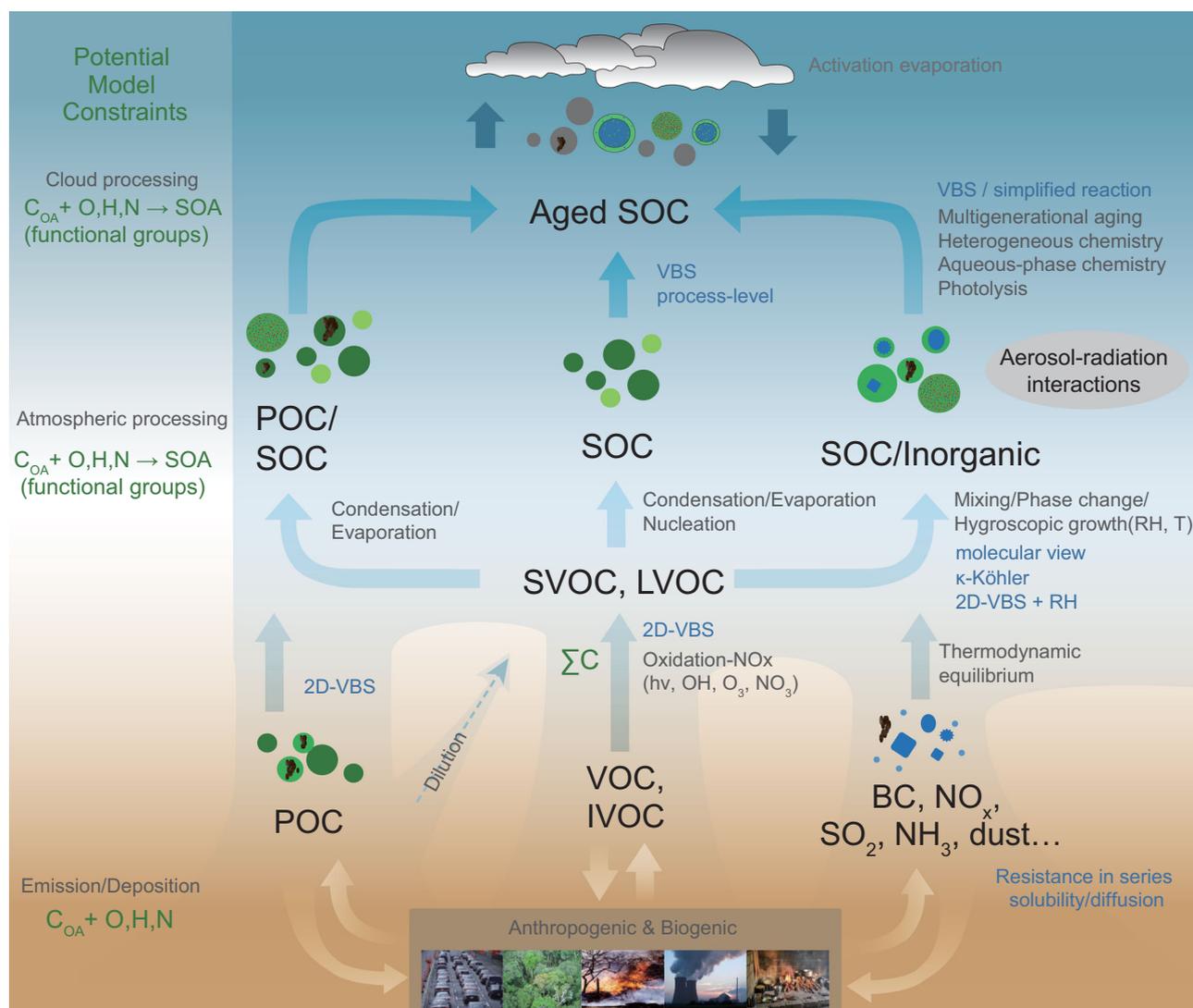


Figure 1. Atmospheric production of SOAs and state-of-the-art SOA modelling methods (blue) as well as potential constraints in future model frameworks (green). POC, SOC, IVOC, SVOC and LVOC stand for primary, secondary, intermediate-volatility, semi-volatile and low-volatility organic carbon, respectively.

especially for the high SOA concentrations during haze events in China. Better SOA modelling frameworks are urgently needed for effective air pollution control, as well as for more accurate evaluation of the climate and health impacts of $PM_{2.5}$.

CURRENT STATUS OF SOA MODELLING

The formation of SOA has been incorporated into chemical transport models since the beginning of the 1990s. Early models represented SOA formation via the absorptive partitioning of surrogate oxidation products of volatile organic compounds (VOC) using SOA yields

determined from smog chamber experiments, but these models underestimated the SOA mass by one to two orders of magnitude. Since then, chamber experiments have shed light on our understanding of SOA formation under atmospheric-relevant conditions. The contributions of oxidation of primary emissions of intermediate-volatility or semi-volatile organic compounds (I/SVOC), heterogeneous and aqueous-phase pathways, multigenerational ageing and the oligomerization of SOA have been incorporated into regional modelling in China [4–7]. Some work shows that the heterogeneous and aqueous formation of isoprene-epoxydiol,

glyoxal and methylglyoxal SOA contribute more than half of the summertime SOA in southern China [4,5]. Simulations that use volatility basis sets (VBS) to represent the multigenerational ageing of I/SVOC and VOC can reduce the normalized mean bias of the predicted mass for surface SOA by 50% [6]. However, these processes still need measurement constraints. Even with an experimentally-constrained ageing framework built on two-dimensional VBS (2D-VBS), the model still underestimates OA loadings by 40% (medium yield scheme) at four long-term observational sites [7]. Such underestimation appears to be common in most parts of China during different

seasons, and is exacerbated during haze events.

FRAMEWORK FOR FUTURE MODELS

Some advanced knowledge has not yet been applied in SOA modelling in China. For instance, particulate water may act as an additional partitioning medium for organic species and affect the microphysical properties (e.g. viscosity) of particles. Some model runs incorporating water uptake by organic species have shown significantly increased mass concentrations of the predicted SOA [8], although a later work that further considered inorganic water and phase separation was unable to reproduce the observed daytime OA mass in the southeast of the USA [9]. In China, high relative humidity and high concentrations of inorganic salts in PM_{2.5} during haze events can lead to hundreds of $\mu\text{g m}^{-3}$ of aerosol liquid water [10], which may have significant impacts on SOA formation. Thus, OA–water interactions should be incorporated into regional modelling in China.

Better constraints on the emissions of primary I/SVOC and on their multi-generational ageing processes are also needed to improve SOA modelling in China. In particular, residential coal and agriculture waste burning are important emission sources in China that have limited emission mitigation. Representing such emissions and their ageing in models is difficult because of the complexity of OA and the limited source-specific measurements. Elemental ratios are promising constraints with which to reduce the chemical complexity of OA. The 2D-VBS framework tracks atomic oxygen–carbon (O:C) ratios as chemical constraints of OA. However, the inclusion of O:C ratios only is insufficient because urban OA may be rich with other elements like hydrogen and nitrogen. For instance, simulations have shown that IVOC can contribute over half of all SOA in eastern China [7]. However, the atomic hydrogen–carbon (H:C) ratios of IVOC-derived SOA are much lower than the observed H:C ratios there [11], suggesting possible overestimation of IVOC-derived SOA in the models.

Nitrogen in OA should also be constrained in the models because both high NO_x emissions and strong photochemical oxidative capacity in China indicate strong production of organic nitrates, which are unlikely to decline substantially in the near future. As the reduction of SO₂ becomes increasingly effective in China, nitrogen-containing species are expected to play a critical role in the formation and fate of SOA by varying radical and oxidant regimes and particle properties (e.g. volatility and hygroscopicity) [2]. Measurements of OA functional groups have become available, and model representation of the functional groups is one step towards the further chemically constrained SOA [12].

Another breakthrough will be the establishment of the fully coupled gas- and particle-phase organic chemistry in models. When we better understand the oxidation products that form SOA (e.g. highly oxygenated molecules (HOMs) detected by advanced time-of-flight chemical ionization mass spectrometry [13]), a unified chemical mechanism based on molecular tracers may be achieved to better represent the composition and physical/chemical properties of SOA. In addition, new particle formation frequently occurs in China. Ambient sulfuric acid concentrations are insufficient to explain the nanoparticle growth that has been observed, whereas HOMs that are involved in nucleation and initial particle growth may affect particle number concentrations in addition to mass [13]. Several groups have started HOMs measurements in China, which may aid the future development of more accurate models. Better representation of the impact of SOA on cloud condensation nuclei concentrations and aerosol radiation within a chemistry- and meteorology-coupled framework may also improve the capability of models to deal with extreme haze events. Future models also need to consider interactions between SOA production and high levels of other pollutants (e.g. ammonia and dust), as well as the changes of SOA properties (e.g. solubility and diffusivity) during atmospheric evolution. Process-level representations of SOA is useful for the incorporation of

processes like fragmentation and organic photolysis into models to improve the simulated spatial distributions of SOA [14].

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