Organic aerosol volatility and viscosity in the North China Plain: contrast between summer and winter

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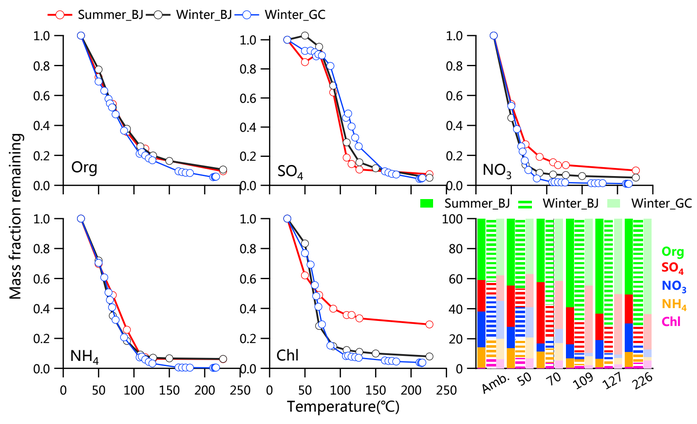
Introduction

- Organic aerosols (OA) account for a substantial mass fraction of atmospheric fine particulate matter. However, the simulation results from chemical transport models often fail to agree with the observations to a certain degree, which is partly due to our limited understanding of chemical mechanisms, reaction rates, and lifetime of OA.
- Volatility and viscosity have substantial impacts on gas-particle partitioning, formation and evolution of aerosol, and hence the predictions of aerosol related air quality and climate effects.
- Previous field observations on volatility distributions of OA are mainly focused on Europe and U.S. under low NO_x levels. The observations in urban and rural areas during wintertime in North China Plain (NCP) under high NO_x levels are very limited.
- Previous studies measured the phase state of bulk aerosol that is generally dominated by hygroscopic secondary inorganic species, our knowledge of the OA phase state and viscosity remains limited.

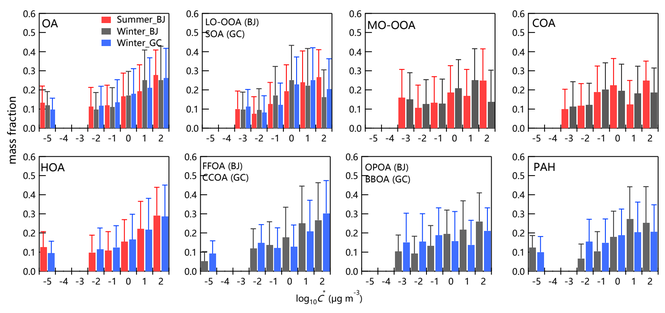
Experimental Methods

- A high-resolution time-of-flight aerosol mass spectrometer (HR-AMS) coupled with a thermodenuder (TD) was deployed in summer (2018/5/20-2018/6/23) and winter (2018/11/25-2018/12/25) at an urban site in Beijing, and a rural site (Gucheng) in winter (2018/12/10-2019/1/13) in NCP .
- The settings of TD heating temperature were 50, 120 (150), and 250 ℃ in summer and winter of 2018 in Beijing. Comparatively, the TD temperature was set to increase linearly in winter at Gucheng site.
- The data were analyzed with positive matrix factorization (PMF) to resolve potential OA factors.
  - Summer2018 in Beijing: hydrocarbon-like OA (HOA), cooking OA (COA), less oxidized oxygenated OA (LO-OOA) and more oxidized OOA (MO-OOA)
  - Winter2018 in Beijing: fossil fuel related OA (FFOA),COA, oxidized POA (OPOA), LO-OOA and MO-OOA
  - Winter2018 in Gucheng: HOA, coal combustion OA (CCOA), biomass burning OA (BBOA) and OOA
- The time-dependent aerosol evaporation in TD was simulated using the dynamic mass transfer model.
  - Six logarithmically spaced effective saturation concentration (C*) bins with the maximum value of 100 μg m^{-3} are used to fit the measured thermograms
  - 6 discrete values of vaporization enthalpy and accommodation coefficient were used, i.e., 20, 50, 80, 100, 150, and 200 kJ mol^{-1}, and 0.01, 0.05, 0.1, 0.2, 0.5, and 1, respectively.
- The glass transition temperature and viscosity of OA were estimated using saturation mass concentration and atomic O/C ratio with the recently developed parameterization formula.

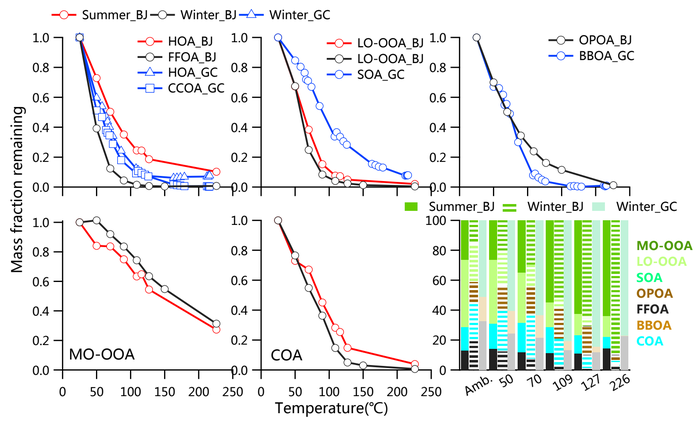
Results and discussion



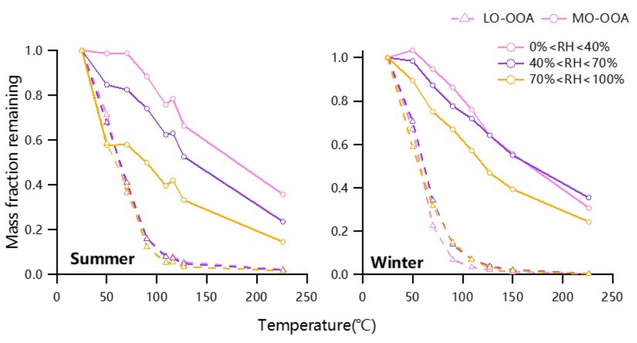
- More remaining nitrate was observed which was more likely caused by the less volatile nitrate in summer, emphasizing the role of organic nitrates (ON) in summer.
- The remaining organics loading in Gucheng was lower than that in Beijing under the same TD temperature during wintertime, particularly at T >150 ℃, suggesting that OA in Gucheng (0.75 μg m^{-3}) was overall more volatile than those at urban sites (0.71 μg m^{-3} in winter vs. 0.55 μg m^{-3} in summer) .
- The volatility distributions of OA varied differently among different OA factors and seasons.

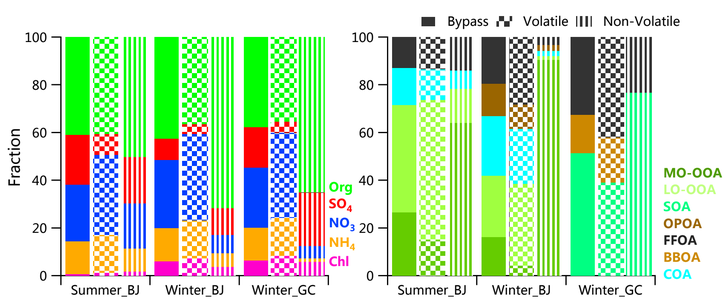


Results and discussion

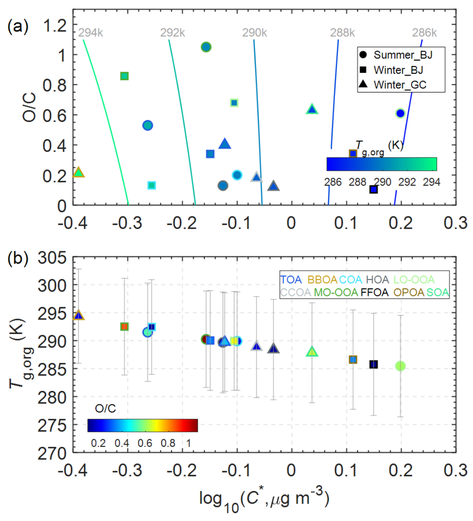


- LO-OOA was more volatile than MO-OOA in summer and winter, consistent with the fact that MO-OOA dominated OA at T > 200 ℃.
- FFOA and CCOA showed lower remaining loadings (~1%) compared to HOA (8-10%) at T > 200℃, implying that HOA contained more non-volatile compounds.
- The volatility of MO-OOA was RH dependent with higher volatility at higher RH levels. These results demonstrated that the composition and formation mechanisms of MO-OOA can be significantly different under different RH levels, yet such chemical information cannot be illustrated by PMF analysis of bulk OA.





- POA dominated volatile OA in winter (61%-62%), while SOA contributed more to volatile OA in summer (74%). Non-volatile OA that is dominated by MO-OOA was highly correlated with BC, and increased as a function of RH, highlighting the potential formation of aqueous-phase SOA on BC.
- The T_g of OA in summer in Beijing (291.5 K) is higher than that in winter (289.7-290.0 K), and both are overall lower than that in Europe and the U.S. The viscosity analysis suggested that OA occurred mainly as solid in winter in Beijing, and the mixing time can be as long as 103 hours because of low temperature and RH, while it dominantly existed in semi-solid phase in Beijing in summer and Gucheng in winter.



Conclusions

- The effective saturation concentration of organic aerosol in summer was smaller than that in winter (0.55 μg m^{-3} vs. 0.71-0.75 μg m^{-3}), indicating that OA in winter in NCP is more volatile due to enhanced primary emissions from coal combustion and biomass burning.
- The MO-OOA showed overall lower volatility than LO-OOA in both summer and winter, yet the volatility of MO-OOA was found to be RH dependent showing more volatile properties at higher RH.
- Our results demonstrated the different composition and chemical formation pathways of MO-OOA under different RH levels.
- the T_g of OA in summer in Beijing (291.5 K) was higher than that in winter (289.7-290.0 K), while it varied greatly among different OA factors.
- The viscosity suggested that OA existed mainly as solid in winter in Beijing (RH = 29±17%), but as semi-solids in Beijing in summer (RH = 48±25%) and Gucheng in winter (RH = 68±24%).
- These results have important implications that kinetically limited gas-particle partitioning may need to be considered when simulating secondary OA formation in NCP.

Acknowledgements

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*A more detailed explanation is available as **aerosol volatility and viscosity in the North China Plain: contrast between summer and winter** (Atmos. Chem. Phys, 21,7, 5463-5476, 2021)*