

Response to Dr. Müller

I find this study very interesting and I can believe that heterogeneous chemistry might have a strong potential for SNA formation in very polluted conditions.

However, I have some doubts regarding the justification for the lower and upper limits used in the RH-dependent expression adopted for the uptake coefficient, γ . The values are taken from studies (K. Wang et al., 2012; Crowley et al., 2010; Shang et al. 2010; Wu et al., 2011) which all concern specifically reactions on dust particles. But haze particles in Northeastern China in winter are primarily a mixture of organic and SNA aerosols, i.e. very different aerosols. Aren't there studies on the uptake by sulfates or organic aerosols? If not, the manuscript should at the very least, state clearly that the adopted uptake coefficients are rather arbitrary – in the case of SO₂, it is chosen in order to match the observed concentrations of sulfates.

Response: We thank Dr. Müller for the insightful comments. It is correct that aerosols during haze episodes in China are mixed particles of organics, dust particles (including anthropogenic dusts), and SNA aerosols. As discussed in Sect. 2.2, we believe that heterogeneous chemistry may play important roles on SNA formation during haze conditions.

In this work, we initially took the uptake coefficient data from dust particles for the following two reasons. First, mineral composition in ambient aerosols in China can come from both anthropogenic and nature sources because of huge emissions of anthropogenic dusts (e.g., ~8 Tg anthropogenic dusts in primary PM_{2.5} emissions in 2005, Lei et al., 2011). As the subsequence, high concentration of mineral compositions was observed in ambient aerosols during polluted days. For example, mineral compositions in PM_{2.5} reached 101.5 $\mu\text{g m}^{-3}$ on 13 Jan 2013 in Beijing (He et al., 2014). In this case, we think that taking the uptake coefficient values from dust aerosols is at least partly valid. Second, in-situ observations have found significant enhancement of SO₂ oxidation rates under wet conditions, indicating possible missing heterogeneous reactions on deliquescent particles (Zheng et al., 2014). However, the coefficients of SO₂ uptake by aerosols are only established for ice surfaces and mineral dust particles (Kolb et al., 2010). The parameterization of heterogeneous reaction of SO₂ on soot, organics, and SNA aerosols are not well established yet. We then took the uptake coefficients from reactions on dust particles and conducted several sensitivity runs by adjusting the uptake coefficients with successive approximation approach. We finally choose the value that can best match observations. We believe that this is the only way to push forward before the proposed mechanism was validated in laboratories. In the revised manuscript, we explained the reasons of using uptake coefficients from reactions on mineral dusts and presented the sensitivity analysis of uptake coefficients.

Another point concerns the abrupt increase in sulfate concentration observed in haze conditions, 70-130 $\mu\text{g m}^{-3}$ in a few hours, which is presented as argument for a large heterogeneous production. Aren't meteorological variations the main driver for such large changes? Although I acknowledge that the larger fraction of SNA in the total aerosol loading is a valid argument to the enhanced SNA formation in haze conditions.

Response: We believe that the abrupt increase of SNA concentrations is mainly due to chemical production rather than meteorological variations although we agree that the stagnant meteorological condition plays an important role on heavy pollution formation. If changes in meteorological conditions dominant the abrupt increase of PM_{2.5}, both primary and secondary components should increase simultaneously. However, significant increase of sulfate/EC ratios was found from clean

conditions to heavily polluted periods, suggesting enhanced chemical productions. It is found that sulfate concentration increased from $3.0 \mu\text{g m}^{-3}$ to $126.5 \mu\text{g m}^{-3}$ (a factor of 40) within three hours on January 12, while element carbon concentration increased from $2.9 \mu\text{g m}^{-3}$ to $10.5 \mu\text{g m}^{-3}$ (a factor of 4) during the same time (Zheng et al., 2014). This suggests that the meteorological variation can only partly interpret the abrupt increase of sulfate concentration, while the main driver of sulfate increase should be attributed to the enhanced chemical formation process, most probably heterogeneous chemistry as discussed in Sect. 2.2.

References:

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