Synergetic formation of secondary inorganic and organic aerosol: Influence of SO_2 and/or NH_3 in the heterogeneous process

(Supporting information)

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Increase of secondary aerosol formation with SO_2 consumption, particle surface area, and particle volume

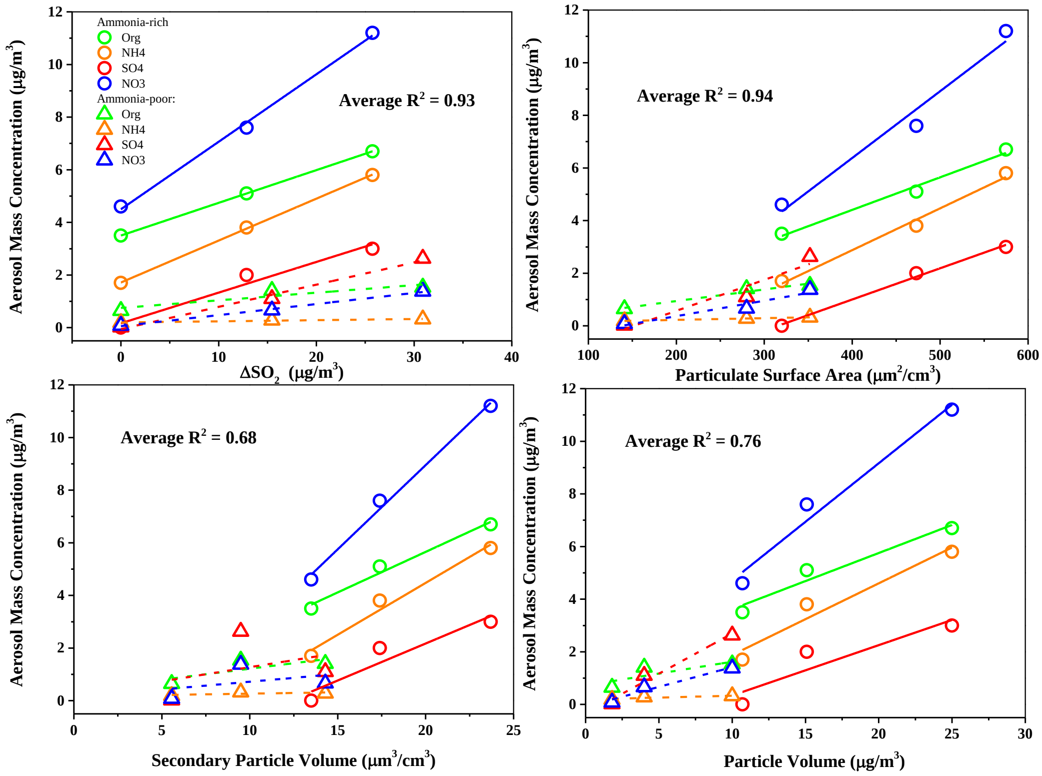

Fig. S1 Correlation of secondary aerosol formation with SO_2 consumption, particle surface area, and particle volume.

Estimating concentrations of nitrogen-containing organics (NOC)

Nitrogen-containing organics (NOC) might contain organonitrates, organic ammonium salts, and species with carbon covalently bonded to nitrogen. Organonitrates could be estimated using methods suggested by Farmer et al. (2010), one of which was using NO_x^+ ratios. The ratio of m/z 30 to m/z 46 for nitrate ($R_{NH_4NO_3}$) is lower than that of organonitrates ($R_{Organonitrates}$) in AMS measurement, so the observed ratio, R_{obs}, can be used to estimate the fraction of the total nitrate signal due to organonitrates (x)

using the Equation S1:

$$x = \frac{\left(R_{obs} \text{-} R_{NH_4NO_3}\right)\left(1 + R_{obs}\right)}{\left(R_{Organonitrates} \text{-} R_{NH_4NO_3}\right)\left(1 + R_{Organonitrates}\right)} \tag{S1}$$

where $R_{NH_4NO_3}$ was measured as 2.35 in the calibration of AMS, and $R_{Organonitrates}$ was assumed to be 15, which was highest value suggested by Farmer et al (2010), to avoid overestimation of organonitrates. The estimated concentrations of organonitrates are shown in Fig. S2.

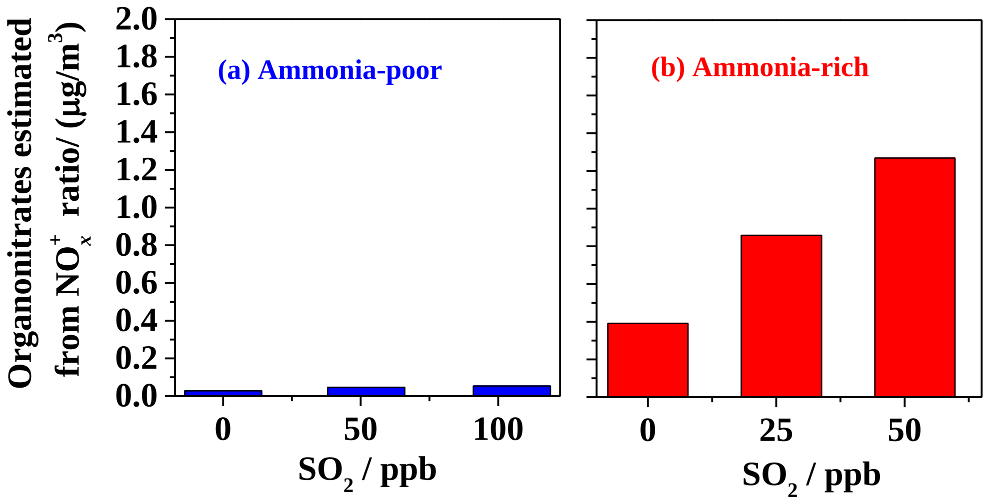

Fig. S2 The estimated concentrations of organonitrates from NO_x^+ ratios as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b) NH_3-rich conditions

As suggested by Farmer et al. (2010), NH_4^+ is required to balance with the SO_4^{2-} and NO_3^- in the absence of NOC. In this study, the measured concentration of NH_4^+ was higher than the calculated concentration according to charge balance, especially in the NH_3-rich experiments. This result indicated the presence of NOC with reduced N (Reduced NOC). The NH_3 present may react with the ring opening oxycarboxylic acids from toluene (Jang and Kamens, 2001) and carbonyl functional group organics (Wang et al., 2010), and result in organic ammonium salt products, imines, imidazole, and so on. The NH_4 balance considering the presence of NOC with reduced N is described by Equation S2:

$$\frac{c_{NH_4}}{18} - \frac{c_{Reduced\ NOC}}{M_{Reduced\ NOC}} = 2\times\frac{c_{SO_4}}{96} + \left[\frac{c_{NO_3}}{62} - \frac{c_{Organonitrates}}{M_{Organonitrates}}\right] \quad (S2)$$

where c_{NH_4} , c_{SO_4} and c_{NO_3} are the mass concentrations of ammonium and sulfate and nitrate in AMS measurement results, respectively; while $c_{Reduced\ NOC}$ and $c_{Organonitrates}$ are the estimated mass concentrations of NOC with reduced N and organonitrates, respectively. $M_{Reduced\ NOC}$ and $M_{Organonitrates}$ in Equation S2 are the molecular weights of NOC with reduced N and organonitrates, and are assumed to be 100 and 200, respectively. $M_{Reduced\ NOC}$ is assumed to have a smaller value than $M_{Organonitrates}$ to avoid overestimation of NOC with reduced N. Using the estimated concentration of organonitrates according to Equation S1, the estimated concentrations of the NOC with reduced N are calculated and displayed in Fig. S3.

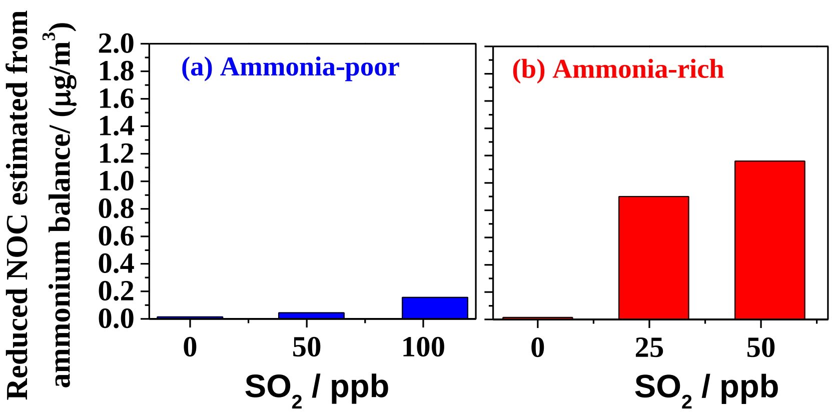

Fig. S3 The estimated concentrations of NOC with reduced N as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b)

NH$_3$-rich conditions

The uncertainty in the results in Fig. S2 and Fig. S3 might be large, since a lot of parameters are assumed and the measurement response of AMS to the NOC is still highly uncertain. We analyzed the organic fragments containing N in the AMS measurements. Farmer et al. (2010) suggested the estimation of concentrations of organonitrates using the sum of the signals of the five major $C_xH_yO_zN^+$ fragments in AMS measurement results. However, as pointed out by Farmer et al (2010) and other studies (Galloway et al., 2009;Laskin et al., 2014;Liu et al., 2015), NOC with reduced N could also produce these fragments. In this study, we used Equation S3 to provide an estimate of NOC:

$$c_{NOC} = \frac{CH_4NO^+ + C_2H_5NO^+ + C_3H_4NO^+ + CH_2NO_3^+ + CH_2NO_2^+}{R_{C_xH_yO_zN^+}} \qquad \text{(S3)}$$

where $R_{C_xH_yO_zN^+}$ is the fraction of these five major $C_xH_yO_zN^+$ fragments and accounts for the total oxidized N signal of the organonitrates samples, and was measured as 0.045 in the study of Farmer et al. (2010). The estimated concentrations of NOC using Equation S3 are shown in Fig. S4. These results appear to be comparable to the sum of organonitrates in Fig. S2 and NOC with reduced N in Fig. S3. Meanwhile, the concentrations of $C_xH_yN^+$ fragments are displayed in Fig. S5. They also have similar change trends with SO_2 concentration as the estimated NOC concentrations.

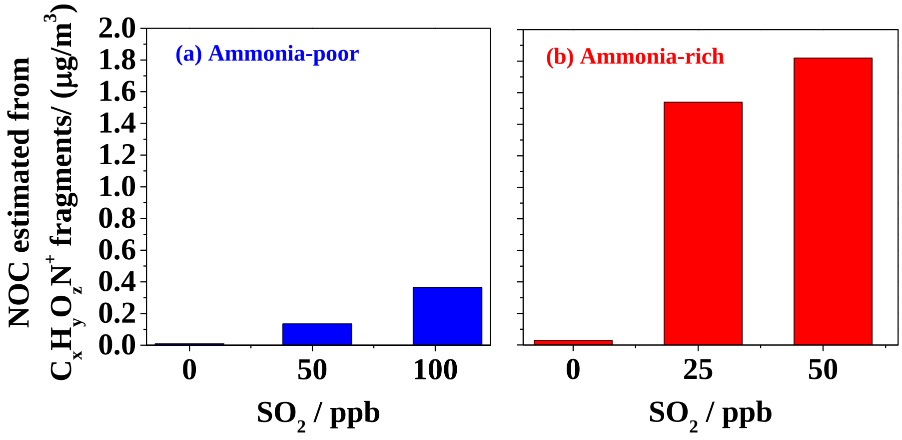

Fig. S4 The estimated concentrations of NOC from $C_xH_yO_zN^+$ fragments as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b) NH_3-rich conditions

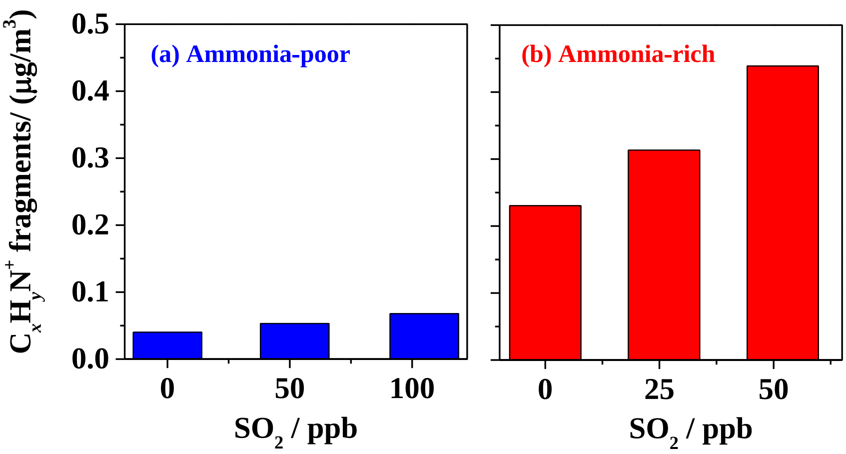

Fig. S5 The concentrations of $C_xH_yN^+$ fragments as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b) NH_3-rich conditions

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