Insights into air pollution chemistry and sulphate formation from nitrous acid (HONO) measurements during haze events in Beijing

SUPPLEMENTARY INFORMATION

Supplementary Figures

Figure S1: Observationally-derived $P_{sulphate}$ values via E2, discounting advection impacts – see text for details.

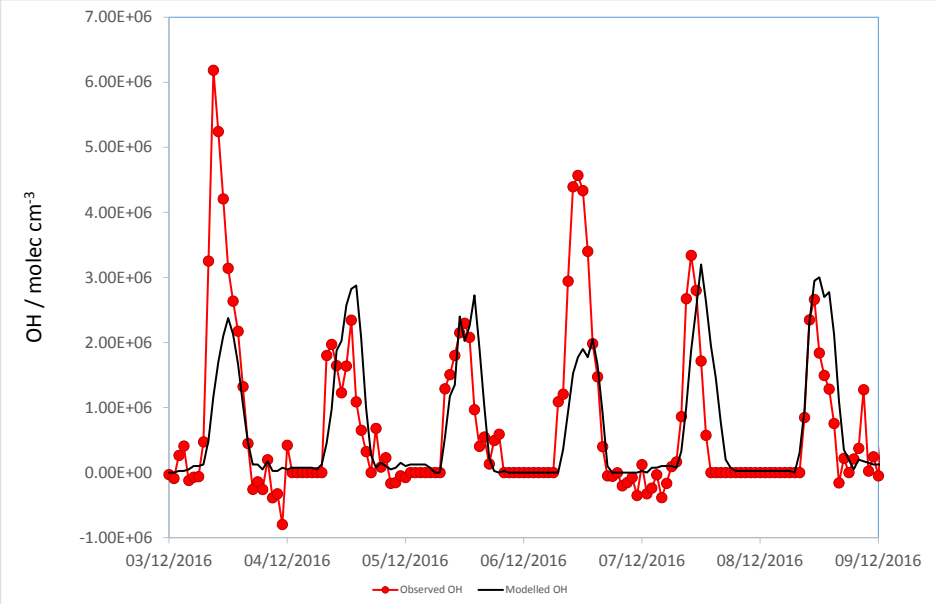

***Figure S2**: Observed (red points) and NAQPMS modelled (black line) OH concentrations*

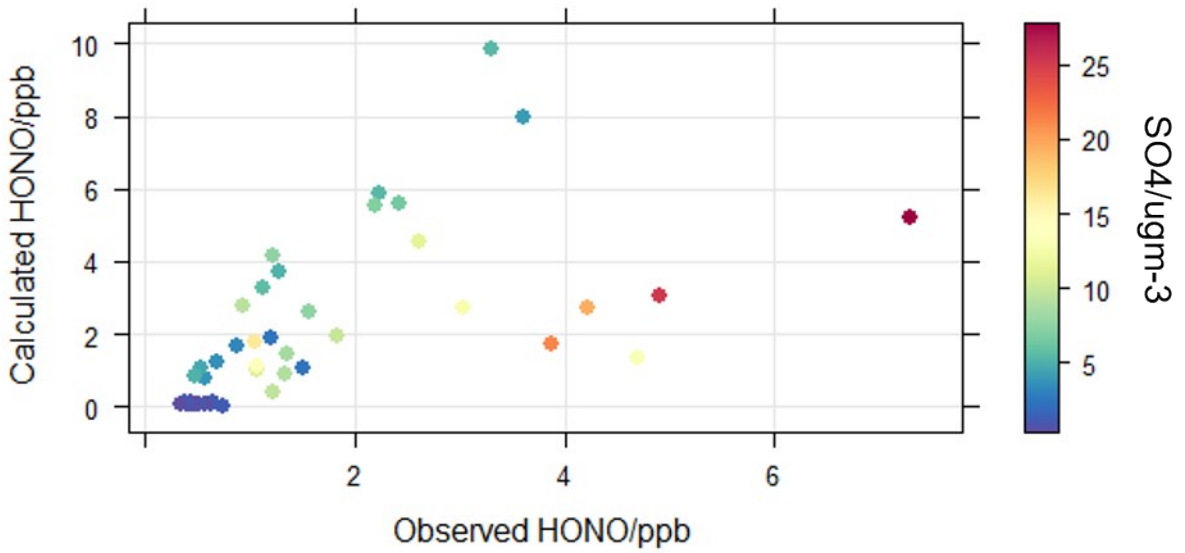

***Figure S3**: Correlation between PSS-calculated and observed HONO mixing ratios, coloured by SO_4 abundance*

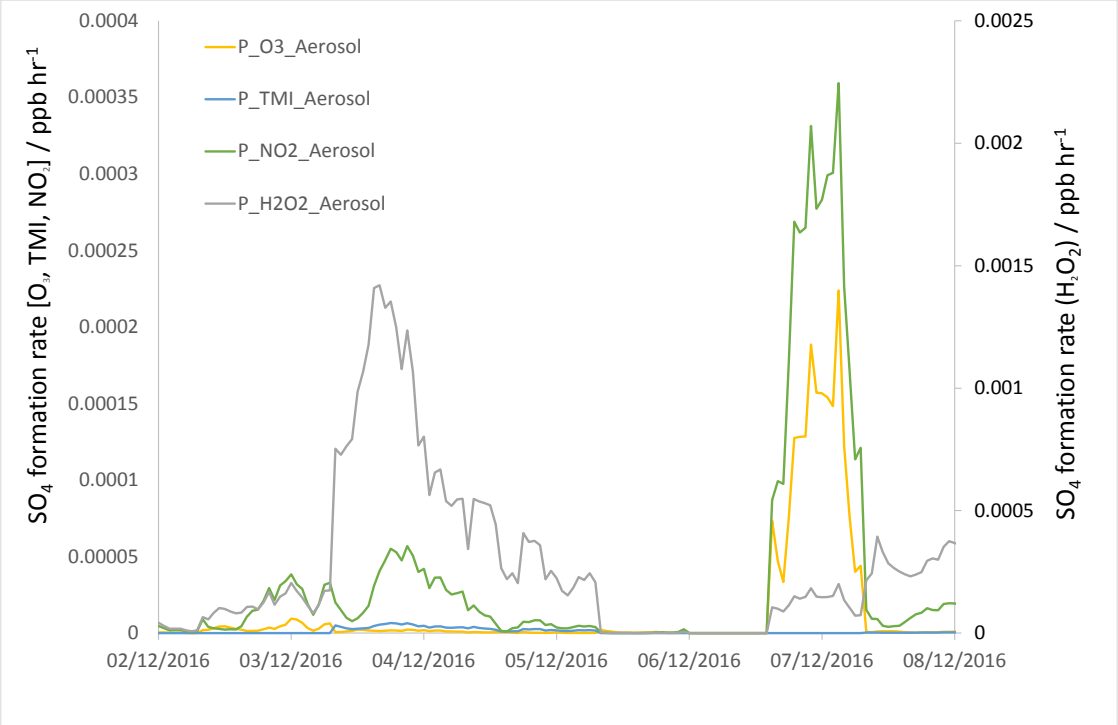

***Figure S4**: Model predicted sulphate formation rates (Ionic strength = zero case) for the H_2O_2, O_3, NO_2 and TMI mechanisms – axis expansion from Figure 6.*

Supplementary Tables:

ST1, ST2 : 24-hour mean observed meteorological parameters, key gas phase mixing rations and aerosol (condensed phase) concentrations

ST3, ST4: Condensed-phase model kinetic parameters adopted

Date	Met. Parameters		Measured mixing ratios / ppb				
	RH / %	Temp / °C	O_3	NO	NO_2	SO_2	NH_3
01/12/2016	24.2	9.3	16.4	6.4	28.5	3.2	10.0
02/12/2016	36.8	7.5	4.8	38.0	45.4	5.9	17.4
03/12/2016	48.0	7.3	5.1	69.5	59.5	9.8	22.5
04/12/2016	57.3	7.2	5.4	67.0	56.4	8.1	22.9
05/12/2016	30.3	6.5	12.6	9.7	24.4	2.7	13.6
06/12/2016	28.9	5.5	3.6	83.7	54.4	7.4	16.7
07/12/2016	39.8	7.5	3.9	88.6	58.1	8.8	22.9
08/12/2016	34.8	8.0	16.8	41.1	28.8	4.9	17.4
09/12/2016	29.4	5.3	13.4	10.7	25.1	3.1	10.4
10/12/2016	38.4	2.0	4.0	36.3	32.0	4.9	14.1

Table ST1*: Measured gas-phase composition and meteorological parameters*

Date	Measured aerosol soluble ion composition / μg m^{-3}							AWC (%)	pH
	K^+	Na^+	NH_4^+	Ca^{2+}	NO_3^-	SO_4^{2-}	Cl^-		
01/12/2016	0.4	0.2	4.3	0.2	5.6	3.0	2.4	1.65	4.92
02/12/2016	0.9	0.6	8.3	0.3	15.0	5.0	3.5	7.60	5.07
03/12/2016	2.7	0.8	22.6	0.4	34.6	24.2	8.2	47.35	4.40
04/12/2016	1.3	0.5	12.1	0.3	21.0	12.7	2.9	18.05	4.35
05/12/2016	0.3	0.2	1.7	0.2	1.7	1.4	1.6	0.34	5.50
06/12/2016	1.2	0.8	8.3	0.3	14.9	3.9	5.0	6.88	5.81
07/12/2016	1.3	0.5	11.5	0.2	17.6	10.6	4.9	14.37	4.62
08/12/2016	0.2	0.1	1.7	0.3	1.9	2.1	1.3	0.57	4.80
09/12/2016	0.5	0.2	2.9	0.2	4.1	2.4	1.9	1.90	5.16
10/12/2016	0.8	0.5	6.0	0.4	7.8	3.4	4.3	-	-

Table ST2*: Measured aerosol composition, AWC and calculated pH*

Equilibrium reaction	H_{298} (M atm^{-1})/ K_{298} (M)[a]	-ΔH/R (K)	Supplementary Information Reference
$SO_2(g) + H_2O \leftrightarrow SO_2 \cdot H_2O$	1.3	3100	1
$SO_2 \cdot H_2O \leftrightarrow HSO_3^- + H^+$	1.3×10^{-2}	1960	2
$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$	6.6×10^{-8}	1500	2
$O_3(g) \leftrightarrow O_3(aq)$	1.13×10^{-2}	2500	1
$H_2O_2(g) \leftrightarrow H_2O_2(aq)$	9.1×10^{4}	6900	1
$NO_2(g) \leftrightarrow NO_2(aq)$	1.3×10^{-2}	2500	1

[a] the temperature dependence is represented by

$$H(T) = H_{298}exp[-\frac{\Delta H}{R}(\frac{1}{T}-\frac{1}{298})]$$

$$K(T) = K_{298}exp[-\frac{\Delta K}{R}(\frac{1}{T}-\frac{1}{298})]$$

Table ST3*: Thermodynamic data for aqueous equilibrium constants*

Reaction	Rate expression (M S^{-1})	Supplementary Information Reference
$SO_2 + H_2O_2 \rightarrow SO_4^{2-} + H_2O$	$k_1[H^+][HSO_3^-][H_2O_2(aq)]/(1+K[H^+])$ $k_{1=7.45\times10^7}\ M^{-1}\ s^{-1}$, E/R [a] =4430K $K = 13M^{-1}$	2
$SO_2 + O_3 \rightarrow SO_4^{2-} + O_2$	$(k_2[SO_2\,H_2O] + k_3[HSO_3^-] + k_4[SO_3^{2-}])\,[O_3(aq)]$ $k_{2=2.4\times10^4}\ M^{-1}\ s^{-1}$ $k_{3=3.7\times10^5}\ M^{-1}\ s^{-1}$, E/R=5530K $k_{4=1.5\times10^9}\ M^{-1}\ s^{-1}$, E/R=5280K	2
$SO_2 + 1/2O_2 \xrightarrow{Mn(II),\ Fe(III)} SO_4^{2-}$	$k_5[H^+]^{-0.74}$[S(IV)] [Mn(II)] [Fe(III)] (pH ≤ 4.2) $k_{5=3.72\times10^7}\ M^{-1}\ s^{-1}$ $k_5[H^+]^{0.67}$[S(IV)] [Mn(II)] [Fe(III)] (pH > 4.2) $k_{5=2.51\times10^{13}}\ M^{-1}\ s^{-1}$	3
$SO_2 + 2NO_2 \rightarrow SO_4^{2-} + 2HONO$	$k_6[NO_2(aq)]$ [S(IV)]] $k_{6=1.4\times10^5}\ M^{-1}\ s^{-1}$, E/R=0K (pH ≤ 5.0) $k_{6=8.4\times10^{-3}}[H^+]^{-1.444}\ M^{-1}\ s^{-1}$, E/R=0K (5.0<pH ≤ 5.8) $k_{6=2.0\times10^6}\ M^{-1}\ s^{-1}$, E/R=0K (pH>$5.8$)	4

[a] the temperature dependence of kinetic constant *k* is represented by

$$k(T) = k_{298}exp[-\frac{E}{R}(\frac{1}{T}-\frac{1}{298})]$$

[b] S(IV) refers to the total dissolved sulphur in solution in oxidation state 4, given by

$$S(IV) = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{2-}]$$

Table ST4*: Rate expression and rate coefficients of aqueous-phase formation of sulphate*

References for Supplementary Tables

1. R. Sander, Atmos. Chem. Phys. 2015, 15, 4399
2. Seinfeld, J.H. and S. N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2016, 3rd Edn, John Wiley & Sons, Inc., Hoboken, New Jersey
3. T. Ibusuki and K. Takeuchi, Atmos. Environ., 1987, 21, 1555
4. Y. Cheng, G. Zheng, C. Wei, Q. Mu, B. Zheng, Z. Wang, M. Gao, Q. Zhang, K. He, G. Carmichael, U. Poschl and H. Su, Sci. Adv., 2016, 2, e1601530