Aerosol aqueous phase oxidation of SO_2 by NO_2 in Chinese haze formation process

Gehui Wang, Jiayuan Wang, Can Wu, Jianjun Li

School of Geographic Sciences,
East China Normal University, Shanghai, China

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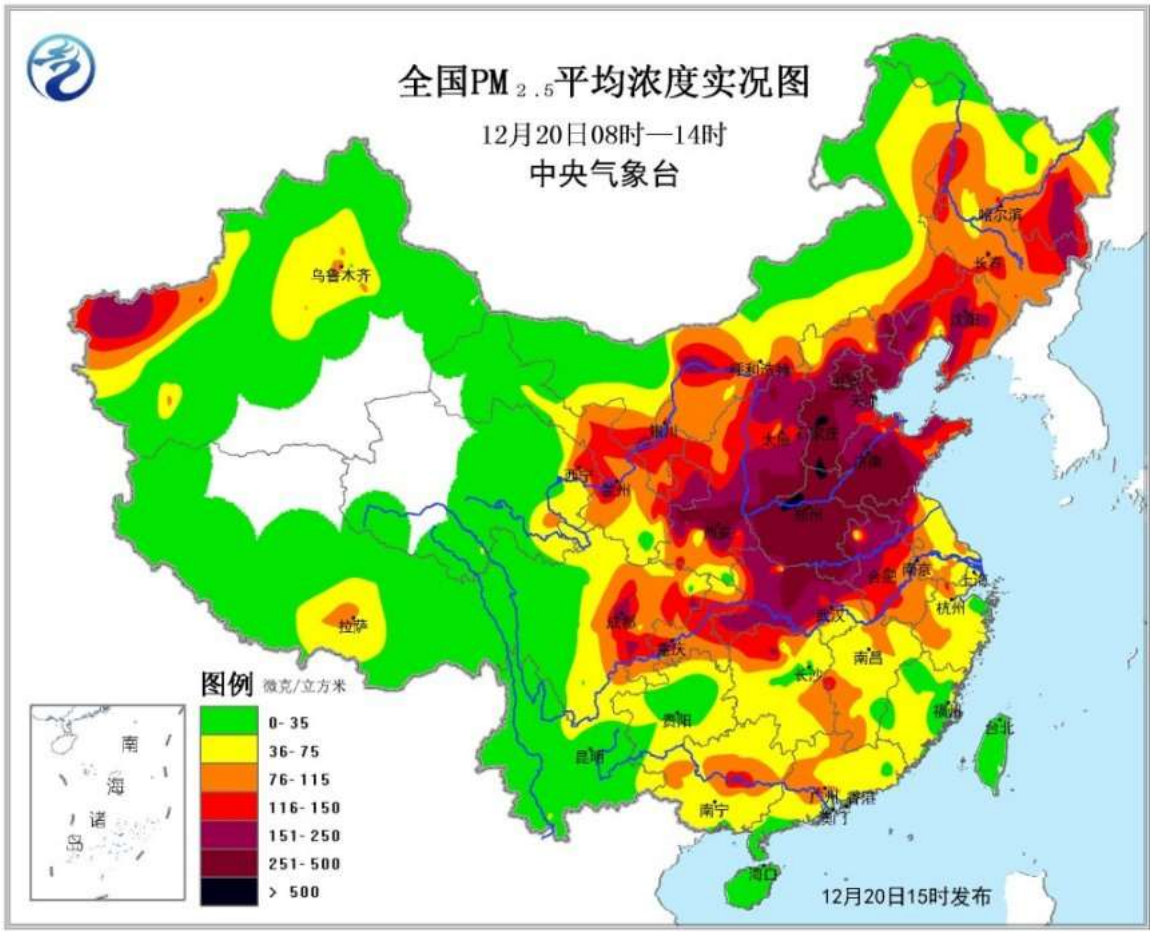
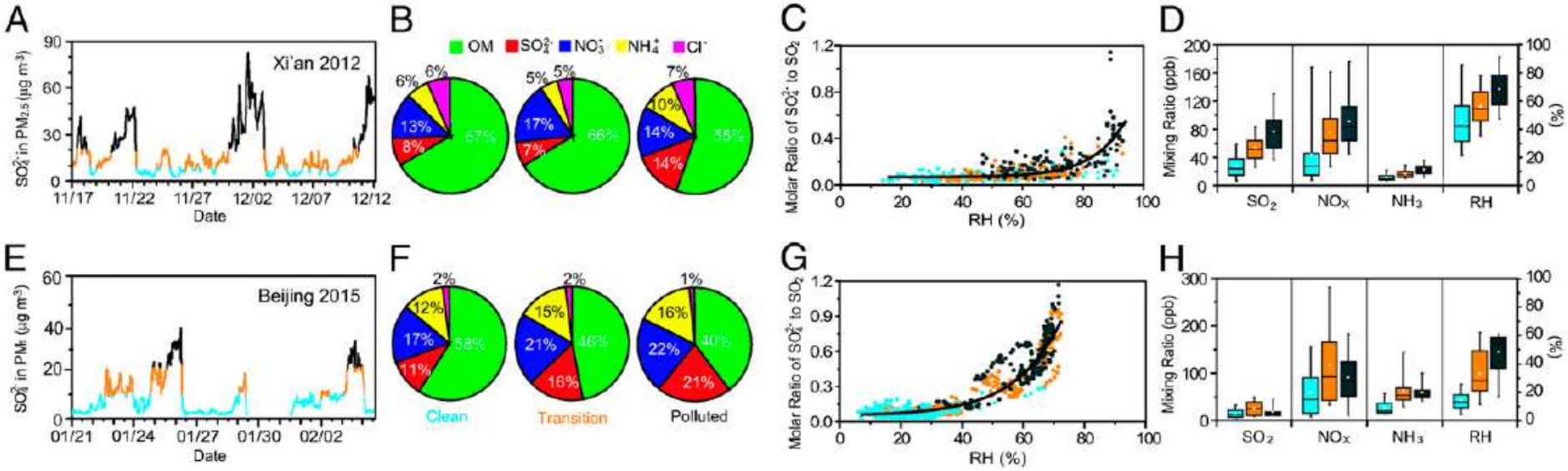
Hourly concentration of $PM_{2.5}$ in China on December 20, 2016



Hourly variation of sulfate in Xi'an and Beijing: Significant aqueous sulfate production

(Wang et al., PNAS 2016)



(1) Clean period： OM (organic matter) dominant Polluted period：inorganic SNA dominant

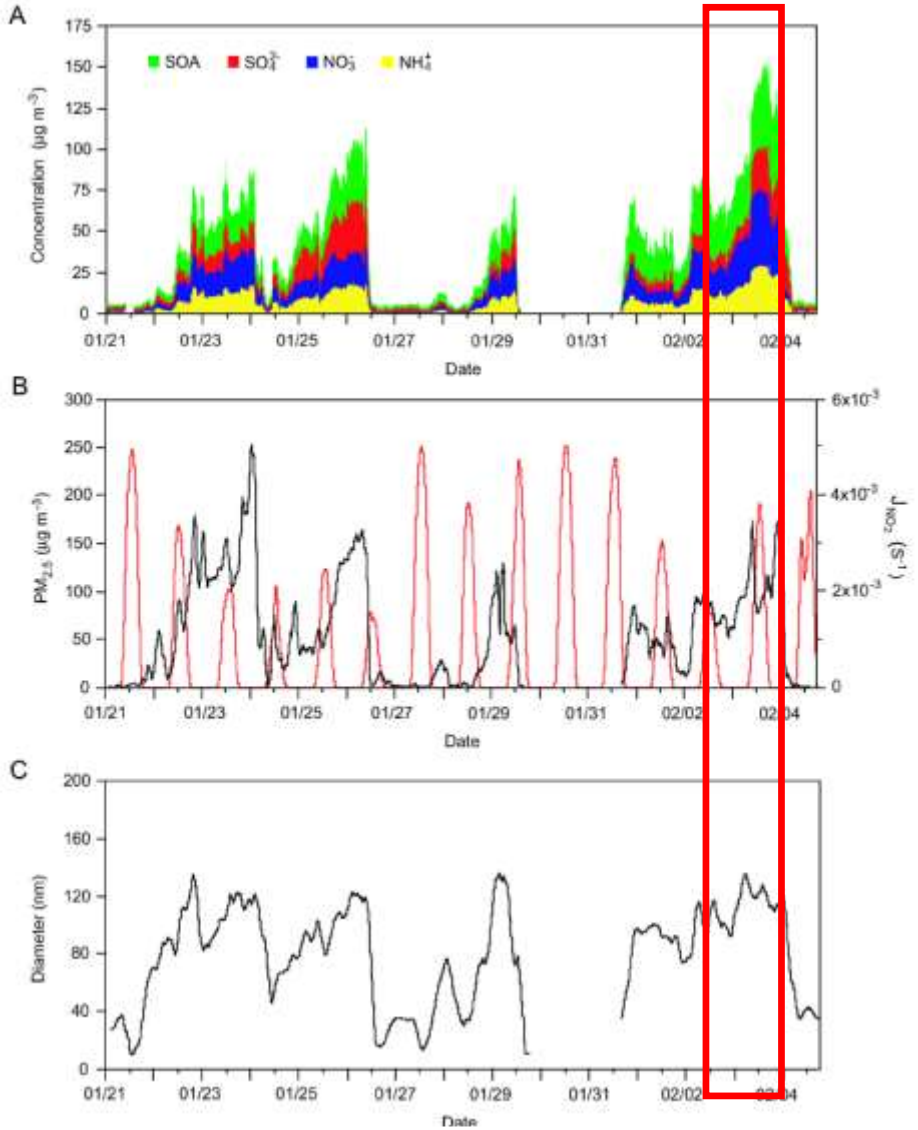
(2) OM in Xi'an more abundant than in Beijing

(3) Sulfate increased exponentially with RH

(4) Rapid conversion of SO2 to SO42- in Beijing under lower RH compared to that in Xi'an

(5) High levels of SO2,NOx and NH3 in haze periods along with high RH

Weak photochemical activity on hazy day: low ozone, reduced visibility



Formation mechanisms of atmospheric sulfate in models

$$OH + SO_2 + M \rightarrow HO_2 + \text{Sulfate}$$ **Gas-phase**

Aqueous phase

$$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O \quad (M4)$$

$$SO_2 + O_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ + O_2 \quad (M5)$$

$$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+ + O_2 \quad (M6)$$

$$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2 \quad (M7)$$

$$SO_2 + H_2O + 0.5O_2 + Fe(III)/Mn(II) \rightarrow SO_4^{2-} + 2H^+ \quad (M8)$$

$$HSO_3^- + CH_3OOH \rightarrow SO_4^{2-} + H^+ + CH_3OH \quad (M9)$$

$$HSO_3^- + CH_3COOOH \rightarrow SO_4^{2-} + H^+ + CH_3COOH \quad (M10)$$

Wang et al., JGR 2014

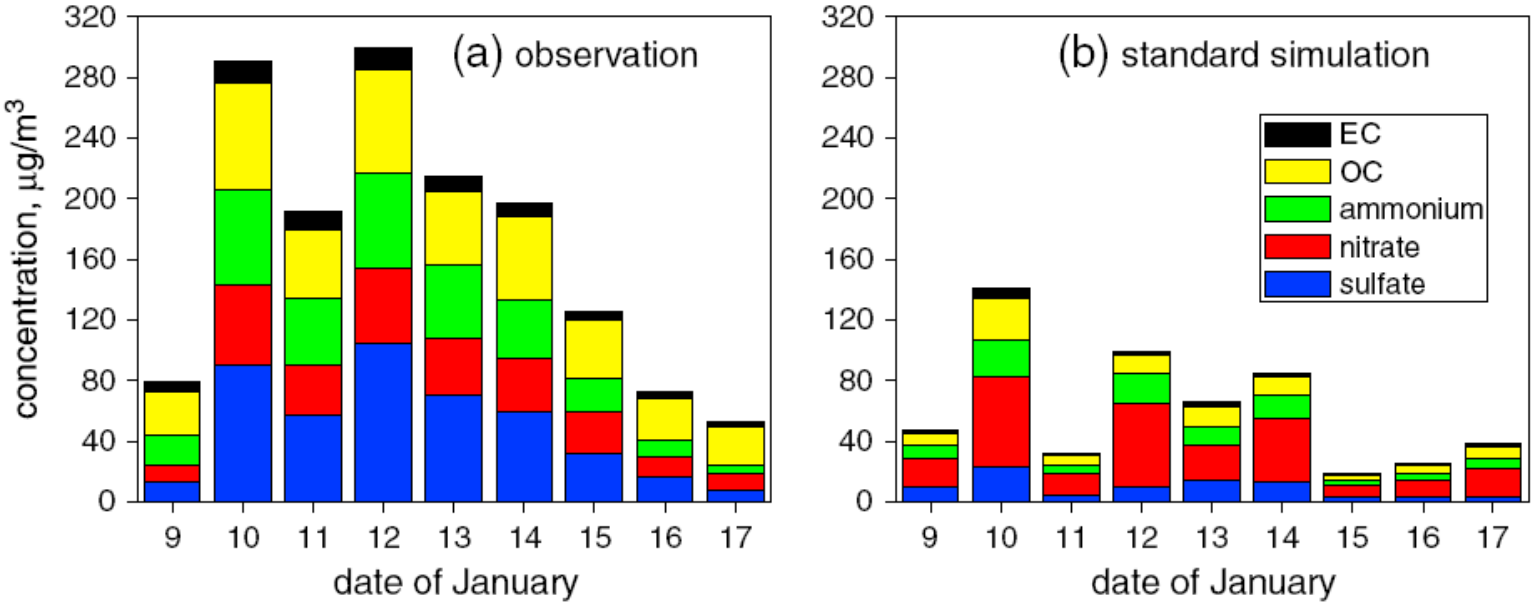
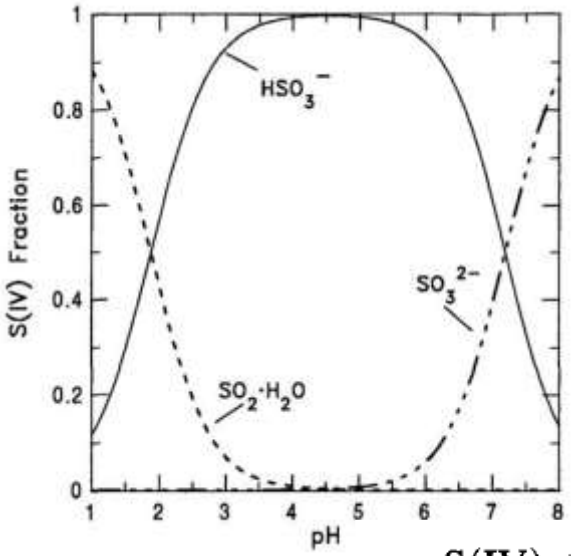
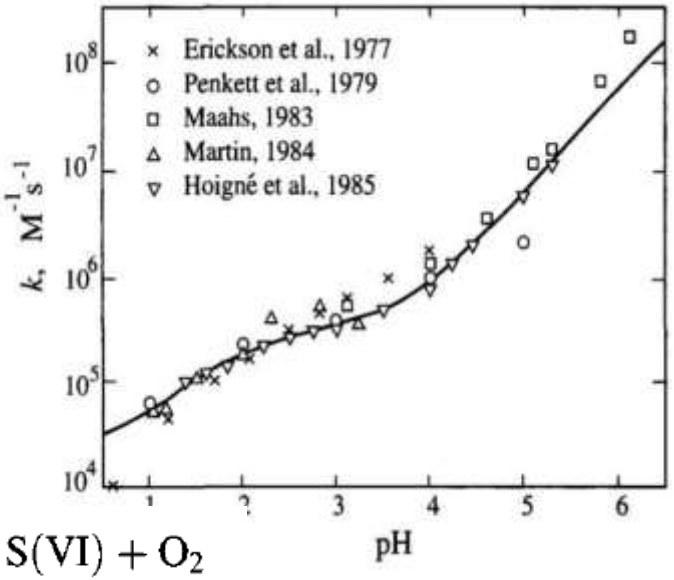


Table 2. A Summary of All the Simulations in This Study

Simulation Name	Description
Standard simulation	Model standard simulation with the 2013 inventory
DoubleSO_2 run	SO_2 emissions from the standard simulation are doubled over NC and reduced by 30% over SC. Changes are applied uniformly throughout January.
Emission_run	Total monthly emissions of SO_2, OC, and EC (anthropogenic portions only) from the standard run are increased by 100% over NC; SO2 emissions over SC are reduced by 30%; NO*x* and NH3 emissions are the same as those in the standard run. The meteorology correction factors are applied on a day-to-day basis to emissions of SO_2, NO*x*, NH_3, OC, and EC over NC.
Gamma_run T1	Emissions are the same as in the emission_run; $\gamma = 10^{-4}$ when RH = 50%, $\gamma = 10^{-3}$ when RH = 50%; γ increases linearly with RH from 50% to 100% (equation (2)).
Gamma_run T2	Emissions are the same as those in the emission_run; $\gamma = 10^{-3}$ when RH = 50%, $\gamma = 10^{-2}$ when RH = 50%; γ increases linearly with RH from 50% to 100% (equation (2)).
Gamma_run T3	Emissions are the same as those in the emission_run; $\gamma = 10^{-2}$ when RH = 50%, $\gamma = 10^{-1}$ when RH = 50%; γ increases linearly with RH from 50% to 100% (equation (2)).

Acidity is key to SO_2 oxidation in aerosol aqueous phase





$$S(IV) + O_3 \rightarrow S(VI) + O_2$$

$$R_0 = -\frac{d[S(IV)]}{dt} = (k_0[SO_2 \cdot H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_3] \qquad (7.80)$$

with $k_0 = 2.4 \pm 1.1 \times 10^4\ M^{-1}\ s^{-1}$, $k_1 = 3.7 \pm 0.7 \times 10^5\ M^{-1}\ s^{-1}$ and, $k_2 = 1.5 \pm 0.6 \times 10^9\ M^{-1}\ s^{-1}$. The activation energies recommended by Hoffmann and Calvert (1985) are based on the work of Erickson et al. (1977) and are $46.0\ kJ\ mol^{-1}$ for k_1 and $43.9\ kJ\ mol^{-1}$ for k_2.

(1) When pH>3.0, SO2 almost entirely exists as HSO3-, SO32-, solubility enhanced

(2) Oxidation rate also sharply increased

Classic Textbook：SO_2 oxidation by NO_2 is unimportant

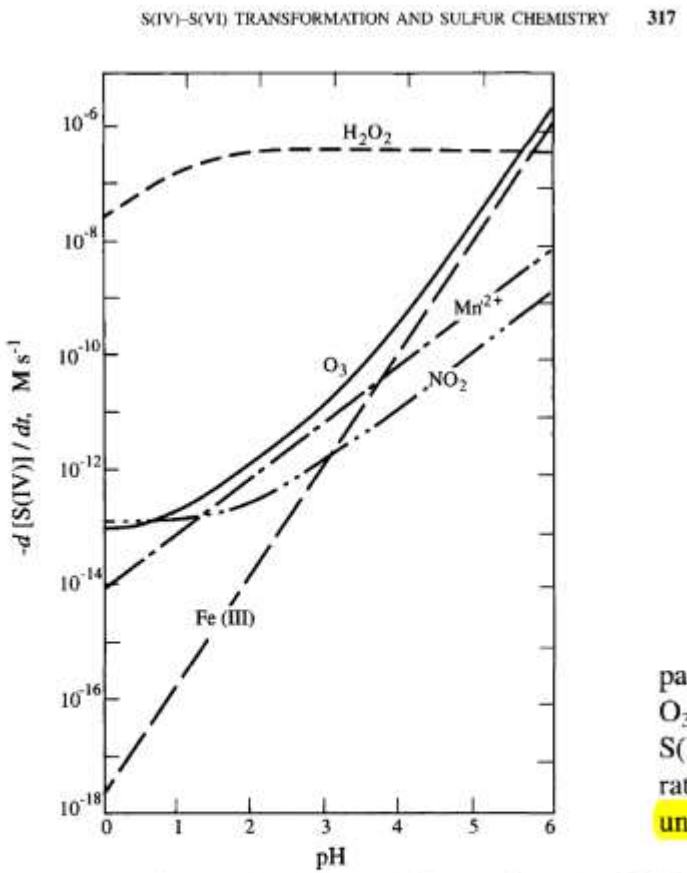
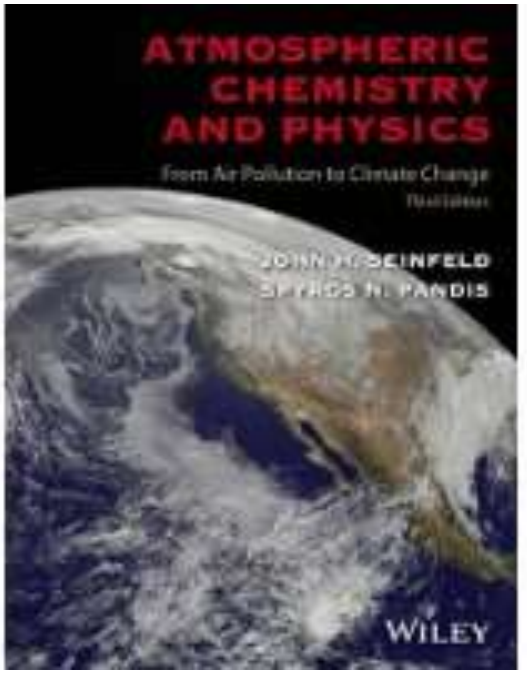


FIGURE 7.19 Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) as a function of pH. Conditions assumed are $[SO_2(g)] = 5$ ppb; $[NO_2(g)] = 1$ ppb; $[H_2O_2(g)] = 1$ ppb; $[O_3(g)] = 50$ ppb; $[Fe(III)] = 0.3\,\mu M$; $[Mn(II)] = 0.03\,\mu M$.

oxidation rates in $\mu M\,h^{-1}$ for the different paths at 298 K for the conditions

$[SO_2(g)] = 5$ ppb	$[H_2O_2(g)] = 1$ ppb
$[NO_2(g)] = 1$ ppb	$[O_3(g)] = 50$ ppb
$[Fe(III)(aq)] = 0.3\,\mu M$	$[Mn(II)(aq)] = 0.03\,\mu M$



We see that under these conditions oxidation by dissolved H_2O_2 is the predominant pathway for sulfate formation at pH values less than roughly 4–5. At pH ≥ 5 oxidation by O_3 starts dominating and at pH 6 it is 10 times faster than that by H_2O_2. Also, oxidation of S(IV) by O_2 catalyzed by Fe and Mn may be important at high pH, but uncertainties in the rate expressions at high pH preclude a definite conclusion. Oxidation of S(IV) by NO_2 is unimportant at all pH for the concentration levels above.

$$2\,NO_2\,(aq) + HSO_3^-\,(aq) + H_2O\,(aq) \rightarrow 3\,H^+(aq) + 2\,NO_2^-\,(aq) + SO_4^{2-}(aq)$$

(Y. N. Lee et al, 1983)

$SO_2 \neq HSO_3^-$

Transition metal ions (Fe/Mn) are negligible

Table S1. Gaseous and PM pollutants and meteorological parameters during Xi'an 2012

	Clean		Transition		Polluted	
	Mean	Range	Mean	Range	Mean	Range
I. Gaseous pollutants (ppb)						
SO_2	28±17	1.0–86	54±22	17–191	78±31	16–203
NO_X	44±49	5.0–264	76±51	15–300	92±39	25–245
O_3	7.4±7.0	0.0–26	4.1±4.7	0.4–11	4.1±2.4	0.6–9.6
NH_3	12±7.4	4.7–67	17±7.7	7.6–35	23±8.3	9.3–61
HONO	1.3±1.0	0.2–5.4	2.1±1.3	0.2–6.5	2.7±1.8	0.3–10
II. Inorganic ions, Fe, Mn and organic matter in $PM_{2.5}$ (μg m^{-3})						
SO_4^{2-}	5.9±2.2	2.3–10	14±4.4	10–20	38±14	20–83
NO_3^-	8.7±4.9	1.4–25	16±6.7	3.8–35	33±10	12–55
Cl^-	4.0±3.7	0.0–22	9.8±5.1	2.4–28	14±6.3	2.6–34
NH_4^+	4.0±2.2	0.8–11	10±3.7	5.1–18	25±7.7	3.2–44
Na^+	3.6±3.2	0.2–8.4	4.5±3.2	0.5–17	4.2±2.7	0.5–17
K^+	1.3±0.7	0.3–4.1	3.1±1.2	1.3–7.0	4.6±1.4	1.8–8.3
Mg^{2+}	0.2±0.1	0.1–0.7	0.3±0.1	0.0–0.7	0.3±0.1	0.0–0.8
Ca^{2+}	1.6±1.0	0.3–6.3	2.4±1.2	0.0–5.3	2.3±1.2	0.2–5.9
Total ions	29±13	6.8–63	60±19	34–97	121±32	65–199
Fe (μg m^{-3})	0.82±0.29	0.37–1.13	1.51±0.70	0.60–3.0	1.76±0.66	0.79–2.79
Mn (μg m^{-3})	0.04±0.04	0.00–0.10	0.11±0.08	0.04–0.35	0.15±0.07	0.08–0.29
Water-soluble Fe (ng m^{-3})	1.5±2.1	0.0–6.1	4.6±3.9	0.0–14	16±5.1	7.3–23
Water-soluble Mn (ng m^{-3})	10±2.1	3.8–20	21±8.7	11–40	41±16	17–70
Organic matter (OM)	35±15	7.0–70	99±33	38–163	177±39	116–288
pH	6.70±1.40	4.43-11.0	6.04±1.24	4.16-8.03	6.96±1.33	4.14-8.16
III. $PM_{2.5}$ and meteorological parameters						
$PM_{2.5}$ (μg m^{-3})	43±18	8.0–74	139±65	76–613	250±120	101–839
T (^OC)	5.7±4.1	-2.0–17	4.1±4.0	-2.3–11	4.1±4.4	-3.1–14
RH (%)	46±18	14–94	56±17	26–93	68±14	41–93
Visibility (km)	8.9±3.4	3.2–17	6.1±2.8	2.4–12	3.2±1.1	1.4–7.2

Experimental simulation : SO_2 (g) oxidation by NO_2 (g) in bulk solution

Lab experiment: in a reaction cell covered with aluminum foil (20ºC)

(1) SO2 (g) + NO2 (g) + H2O

(2) SO2 (g) + NO2 (g) + NH3·H2O (3%)

Table S3. Detection of sulfate formation in the reaction cell

Experimental run	SO_2 (350 ppm)	NO_2 (350 ppm)	Water	3 wt % NH_3	Integrated sulfate desorption peak area (x 10^6 cps)
1 (3)	In N_2	In N_2	√	x	6.8±2.6
2 (3)	In N_2	In N_2	x	√	11.0 ±4.3
3 (1)	In air	In air	√	x	6.5
4 (1)	In air	In air	x	√	10.0

The symbols "√" and "x" indicate whether a water or NH_3 solution was used and not used in the exposure, respectively. The number in parenthesis on the right column denotes the number of repeating experiments.

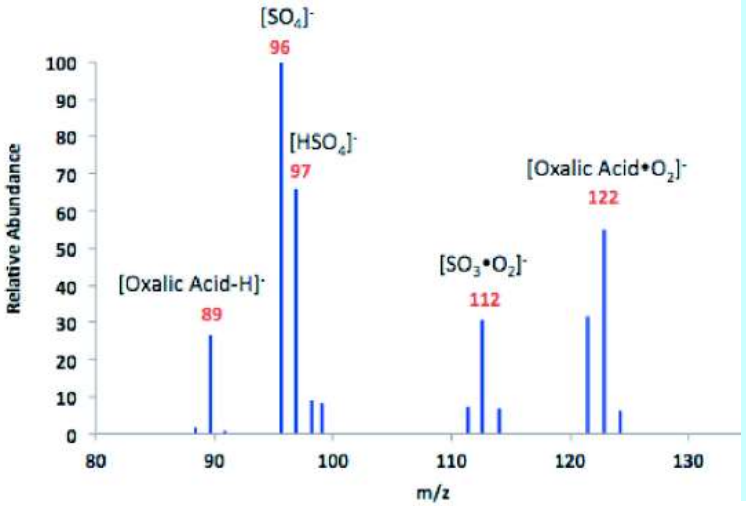
Results and conclusion:

(1) SO_2 can rapidly be oxidized by NO_2 into SO_4^{2-}

(2) NH_3 could promote the reaction

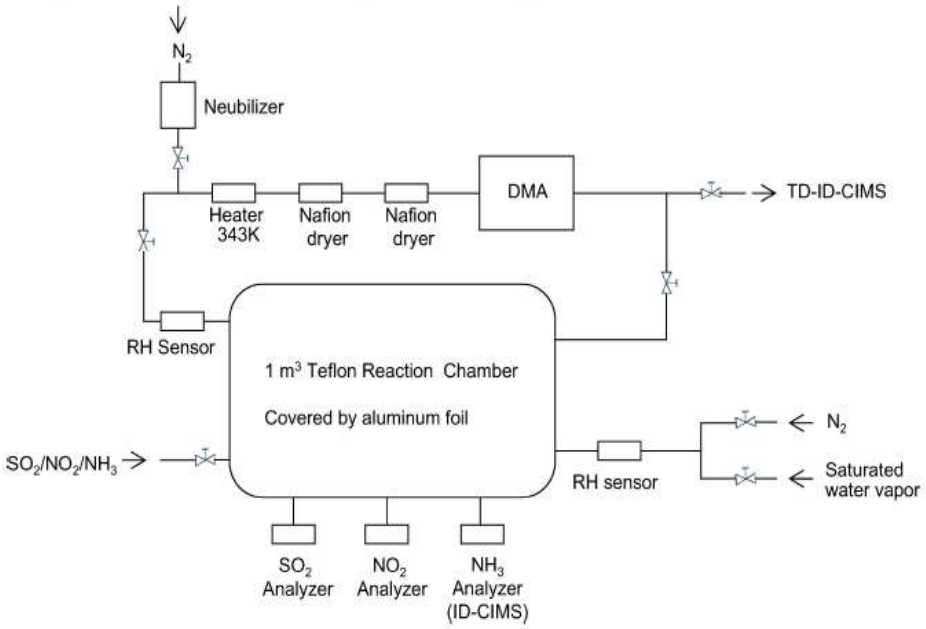
(3) O_2 does not take an important role in the SO_2 conversion process

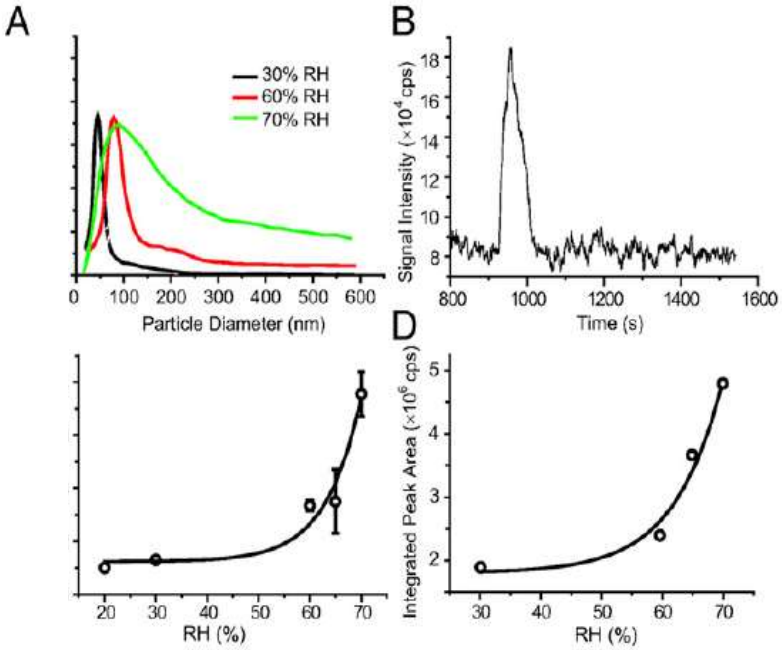
Smog chamber simulation : SO_2+NO_2



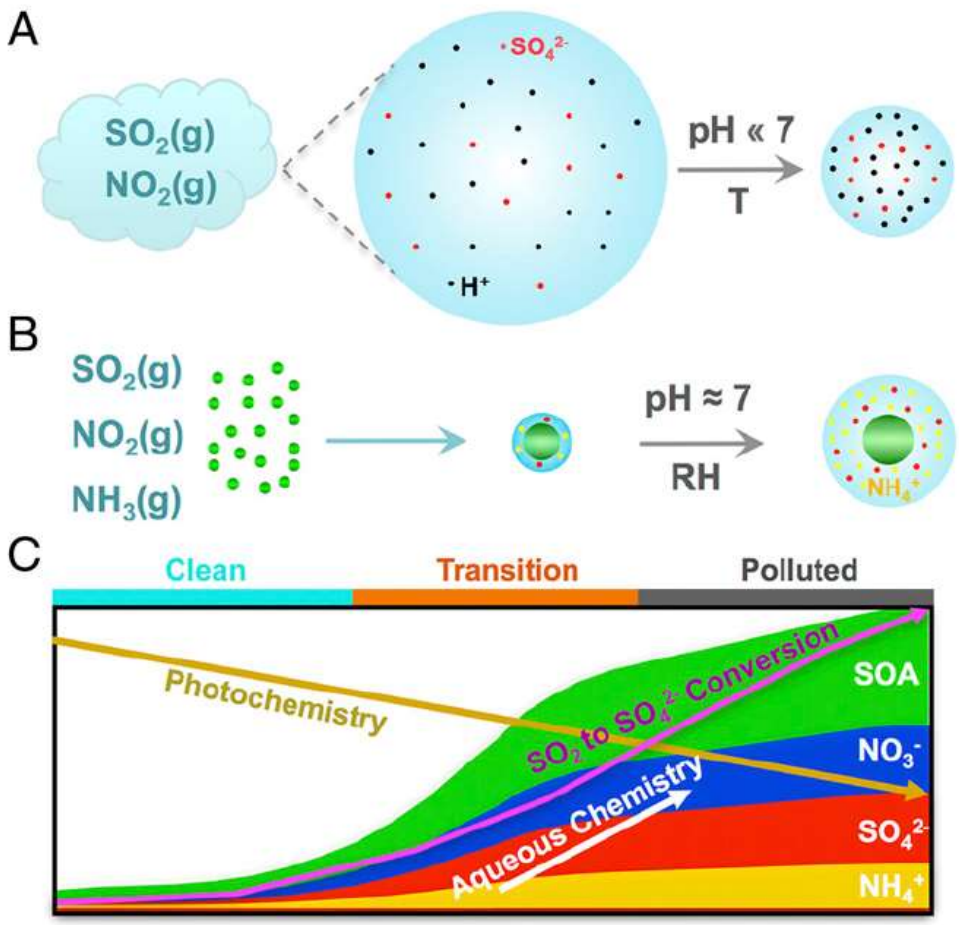
Using 1 m3 PTFE chamber covered completely with aluminium foil:
(1) 45 nm seed (oxalic acid)
(2)100 ppm SO2/NO2/NH3 under different RH conditions for 1 hour
Measure the dry particle size before and after the reaction/ detect the chemical composition

Size growth and sulfate signal can only be seen when seeds, SO2,NO2, NH3 and high RH are all available for the reaction





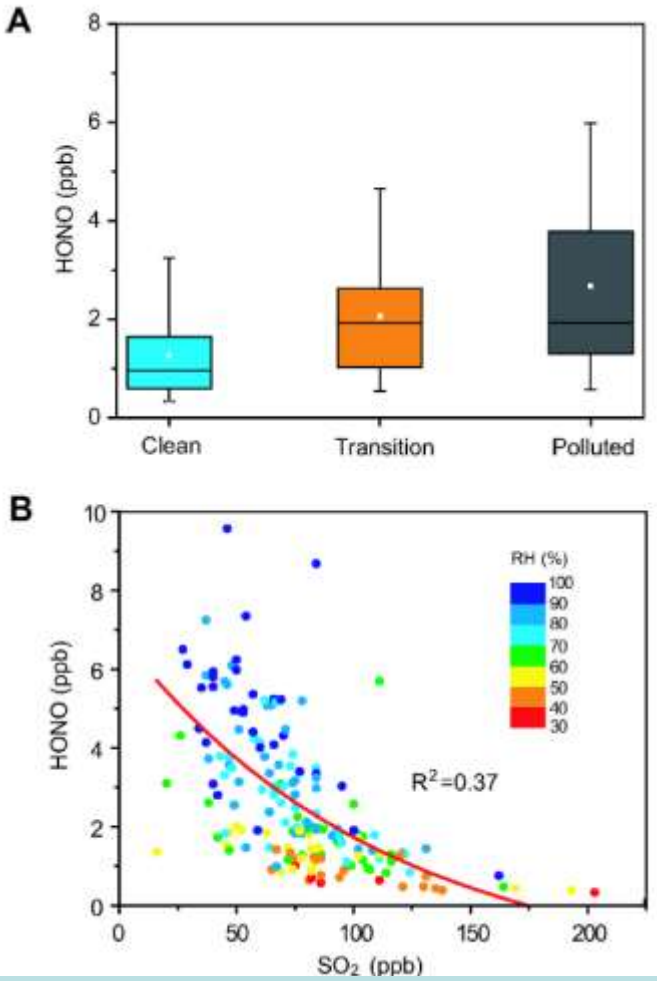
London Fog vs Chinese Haze



$$SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) + 2HONO(g) \quad (A)$$

$$2NH_3(g) + SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq) + 2HONO(g) \ (B)$$

Wang et al., PNAS 2016
"Persistent sulfate formation from Lodon fog to Chinese haze"



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Persistent sulfate formation from London Fog to Chinese haze

Gehui Wang[a,b,c,d,e,1], Renyi Zhang[d,f,1,2], Mario E. Gomez[d,g,1], Lingxiao Yang[a,b], Misti Levy Zamora[d], Min Hu[a], Yun Lin[a], Jianfei Peng[a,b], Song Guo[a,b], Jingjing Meng[a,b,i], Jianjun Li[a,b], Chunlei Cheng[a,b,i], Tafeng Hu[a,b], Yanqin Ren[a,b,i], Yuesi Wang[a], Jian Gao[a], Junji Cao[a,b], Zhisheng An[a,b,i], Weijian Zhou[a,b,i], Guohui Li[a,b], Jiayuan Wang[a,b,i], Pengfei Tian[a,b], Wilmarie Marrero-Ortiz[d,g], Jeremiah Secrest[d,g], Zhuofei Du[f], Jing Zheng[f], Dongjie Shang[f], Limin Zeng[f], Min Shao[f], Weigang Wang[a,b,j], Yao Huang[a,b,i], Yuan Wang[d], Yujiao Zhu[a,i], Yixin Li[f], Jiaxi Hu[f], Bowen Pan[f], Li Cai[k], Yuting Cheng[a,b,i], Yuemeng Ji[a,l], Fang Zhang[d], Daniel Rosenfeld[d,m], Peter S. Liss[n,o], Robert A. Duce[p], Charles E. Kolb[d,q], and Mario J. Molina[d,2]

[a]State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China; [b]Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China; [c]Department of Atmospheric Sciences, Texas A&M University, College Station, TX 77843; [d]Department of Chemistry, Texas A&M University, College Station, TX 77843; [e]School of Geographic Sciences, East China Normal University, Shanghai 200062, China; [f]State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China; [g]Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199; [h]School of Environmental Science and Engineering, Shandong University, Jinan 250100, China; [i]University of Chinese Academy of Sciences, Beijing 100049, China; [j]Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China; [k]Chinese Research Academy of Environmental Sciences, Beijing 100012, China; [l]Beijing Normal University, Beijing 100875, China; [m]Xi'an Jiaotong University, Xi'an 710049, China; [n]Key Laboratory for Semi-Arid Climate Change of the Ministry of Education, College of Atmospheric Sciences, Lanzhou University, Lanzhou 730000, China; [o]State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; [p]Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; [q]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91125; [r]Key Laboratory of Marine Environmental Science and Ecology, Ministry of Education, Ocean University of China, Qingdao 266100, China; [s]School of Electrical Engineering, Wuhan University, Wuhan 430072, China; [t]School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China; [u]Program of Atmospheric Sciences, Institute of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem 91904, Israel; [v]School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, United Kingdom; [w]Aerodyne Research, Inc., Billerica, MA 01821-3976; and [x]Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92092

Contributed by Mario J. Molina, October 9, 2016 (sent for review July 6, 2016; reviewed by Zhanqing Li and Sasha Madronich)

Sulfate aerosols exert profound impacts on human and ecosystem health, weather, and climate, but their formation mechanism remains uncertain. Atmospheric models consistently underpredict sulfate levels under diverse environmental conditions. From atmospheric measurements in two Chinese megacities and complementary laboratory experiments, we show that the aqueous oxidation of SO_2 by NO_2 is key to efficient sulfate formation but is only feasible under two atmospheric conditions: on fine aerosols with high relative humidity and NH_3 neutralization or under cloud conditions. Under polluted environments, the SO_2 oxidation process leads to large sulfate production rates and promotes formation of nitrate and organic matter on aqueous particles, exacerbating severe haze development. Effective haze mitigation is achievable by intervening in the sulfate formation process with reduced NH_3 and NO_2 control measures. In addition to explaining the polluted episodes currently occurring in China and during the 1952 London Fog, this sulfate production mechanism is widespread, and our results suggest a way to tackle this growing problem in China and much of the developing world.

sulfate aerosol | severe haze | pollution | human health | climate

Fine particulate matter (PM), which typically contains a complex mixture of inorganic and organic species, has important implications for several environmental issues (1–3). Presently, the mechanisms leading to PM formation remain uncertain, particularly under highly polluted conditions, hindering efforts in developing effective mitigation policies to reduce their local, regional, and global impacts (1). It is well established, though, that sulfate (SO_4^{2-}) is ubiquitous and is a key PM constituent in the atmosphere. Moreover, hygroscopic sulfate aerosols serve as efficient cloud condensation nuclei, affecting cloud formation, precipitation, and climate (4–8). A major fraction of regional acid deposition is attributed to the sulfate content that exerts debilitating effects on acid-sensitive ecosystems (9). Furthermore, high levels of fine PM have been implicated in adverse human health issues (1), as exemplified by high fatality during the 1952 London Fog (1, 10). Sulfur compounds are emitted globally from many natural and anthropogenic sources (1–3, 11), and there have been high SO_2 emissions from combustion of coal and petroleum products in developing countries (such as China) spurred on by fast economic development (12).

Gaseous SO_2 is converted to particulate sulfate through gas-phase oxidation or aqueous reactions, but the detailed chemical mechanisms remain controversial (1–3, 13, 14). The gas-phase

Significance

Exceedingly high levels of fine particulate matter (PM) occur frequently in China, but the mechanism of severe haze formation remains unclear. From atmospheric measurements in two Chinese megacities and laboratory experiments, we show that the oxidation of SO_2 by NO_2 occurs efficiently in aqueous media under two polluted conditions: first, during the formation of the 1952 London Fog via in-cloud oxidation; and second, on fine PM with NH_3 neutralization during severe haze in China. We suggest that effective haze mitigation is achievable by intervening in the sulfate formation process with NH_3 and NO_2 emission control measures. Hence, our results explain the outstanding sulfur problem during the historic London fog formation and elucidate the chemical mechanism of severe haze in China.

Author contributions: G.W. and R.Z. designed research; G.W., R.Z., M.E.G., L.Y., M.L.Z., M.H., Y. Lin, J.P., S.G., J.M., J.L., C.C., T.H., Y.R., Y.S.W., J.G., J.C., Z.A., W.Z., G.L., J.S., L.Z., M.S., W.W., Y.H., L.C., D.R., P.S.L., R.A.D., C.E.K., and M.J.M. analyzed data; and G.W. and R.Z. wrote the paper.

Reviewers: Z.L., University of Maryland; and S.M., National Center for Atmospheric Research.

The authors declare no conflict of interest.

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To whom correspondence may be addressed. Email: rzhang@tamu.edu or mjmolina@ucsd.edu.

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$$2NH_3(g) + SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq) + 2HONO(g) \quad (1)$$

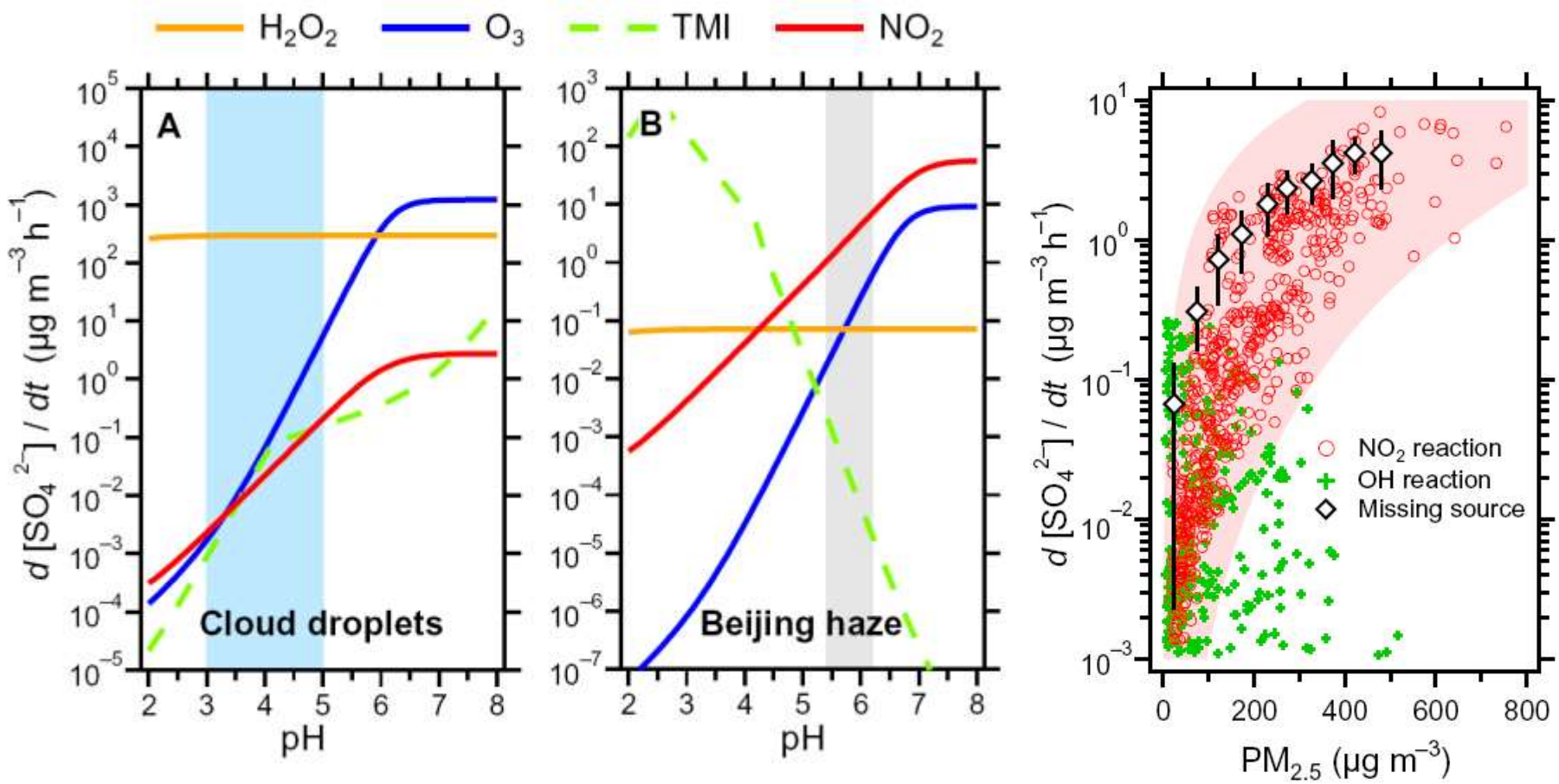
$$SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) + 2HONO(g) \quad (2)$$

Table S5. Uptake coefficient (γ) of SO_2 on aerosols during Beijing 2015

	Average $[SO_4^{2-}]$ ($\mu g\ m^{-3}$)	RH (%)	N ($x10^4$) (cm^{-3})	Average D_p (nm)	S ($\times10^{-5}$) ($cm^2\ cm^{-3}$)	$[SO_2(g)]$ (ppb)	$d[SO_4^{2-}]$ ($\mu g\ m^{-3}$)	dt (hr)	$\gamma \pm 1\sigma$
Clean	4	21	7.5	75.0	1.3	16.3	3.0	7.2	$(1.6\pm0.7)\times10^{-5}$
Transition	14	41	9.0	114.2	3.7	24.2	12.7	6.0	$(2.1\pm1.6)\times10^{-5}$
Polluted	26	56	8.1	116.2	3.4	16.2	14.7	7.0	$(4.5\pm1.1)\times10^{-5}$

Table S6. Uptake coefficient (γ) of SO_2 on oxalic acid particles in the reaction chamber

RH (%)	D_o (nm)	D_p/D_o	N (cm^{-3})	S ($\times10^{-5}$) ($cm^2\ cm^{-3}$)	$[SO_2(g)]$ (ppb)	dt (min)	$\gamma \pm 1\sigma$
30	45	1.06	1.0×10^3	1.3	250	60	$(6.7\pm9.1)\times10^{-6}$
65	45	1.5	1.0×10^3	4.0	250	60	$(8.3\pm5.7)\times10^{-5}$
70	45	2.31	1.0×10^3	3.4	250	60	$(3.9\pm1.2)\times10^{-4}$



Cheng et al., Science Advances (2016)

Max Plank Institute of Chemistry: Dr. Chen et al using WRF-CMAQ model to simulate the aqueous production of SO42-, demonstrating the most important role of SO2 oxidation by NO2 in Beijing haze formation process

Thank you for your attention !