

Supplementary materials of

Summertime fine particulate nitrate pollution in the North China Plain: Increasing trends, formation mechanisms, and implications for control policy

Liang Wen¹, Likun Xue^{1*}, Xinfeng Wang¹, Caihong Xu¹, Tianshu Chen¹, Lingxiao Yang¹, Tao Wang², Wenxing Wang¹

¹ Environment Research Institute, Shandong University, Ji'nan, Shandong, China

² Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, China,

*Corresponding author: L. K. Xue, xuelikun@sdu.edu.cn

Page 1 Cover page

Page 2 *Table S1*

Page 3 *Table S2*

Page 4 *Table S3 and S4*

Table S1. The chemical reactions related to nitrate formation in the RACM/CAPRAM.

No.	Categorized pathways	Reactions
1	HNO ₃ partitioning	HNO ₃ = H ⁺ + NO ₃ ⁻
2		N ₂ O ₅ + H ₂ O = 2H ⁺ + 2NO ₃ ⁻
3	N ₂ O ₅ hydrolysis	N ₂ O ₅ = NO ₂ ⁺ + NO ₃ ⁻
4		NO ₂ ⁺ + H ₂ O = NO ₃ ⁻ + 2H ⁺
5		NO ₃ · + OH ⁻ = NO ₃ ⁻ + OH ·
6		NO ₃ · + Fe ²⁺ = NO ₃ ⁻ + Fe ³⁺
7		NO ₃ · + Mn ²⁺ = NO ₃ ⁻ + Mn ³⁺
8		NO ₃ · + H ₂ O ₂ = NO ₃ ⁻ + H ⁺ + HO ₂ ·
9		NO ₃ · + CH ₃ O ₂ H = NO ₃ ⁻ + H ⁺ + CH ₃ O ₂ ·
10		NO ₃ · + HO ₂ · = NO ₃ ⁻ + H ⁺ + O ₂ ·
11		NO ₃ · + O ₂ ⁻ = NO ₃ ⁻ + O ₂ ·
12		NO ₃ · + HSO ₃ ⁻ = NO ₃ ⁻ + H ⁺ + SO ₃ ⁻
13		NO ₃ · + SO ₃ ²⁻ = NO ₃ ⁻ + SO ₃ ⁻
14		NO ₃ · + HSO ₄ ⁻ = NO ₃ ⁻ + H ⁺ + SO ₄ ⁻
15		NO ₃ · + SO ₄ ²⁻ = NO ₃ ⁻ + SO ₄ ⁻
16		NO ₂ ⁻ + NO ₃ · = NO ₃ ⁻ + NO ₂ ·
17		OHCH ₂ SO ₃ ⁻ + NO ₃ · = NO ₃ ⁻ + OHCH ₂ SO ₃ ·
18	NO ₃ radical aqueous-phase reactions	CH ₃ OH + NO ₃ · = NO ₃ ⁻ + H ⁺ + CH ₂ OH ·
19		CH ₃ CH ₂ OH + NO ₃ · = NO ₃ ⁻ + H ⁺ + CH ₃ CHOH ·
20		CH ₂ (OH) ₂ + NO ₃ · = NO ₃ ⁻ + H ⁺ + CH(OH) ₂ ·
21		CH ₃ CH(OH) ₂ + NO ₃ · = NO ₃ ⁻ + H ⁺ + CH ₃ C(OH) ₂ ·
22		CH ₃ CHO + NO ₃ · = NO ₃ ⁻ + H ⁺ + CH ₃ CO ·
23		HCOOH + NO ₃ · = NO ₃ ⁻ + H ⁺ + CO ₂ H ·
24		HCOO ⁻ + NO ₃ · = NO ₃ ⁻ + CO ₂ H ·
25		CH ₃ COOH + NO ₃ · = NO ₃ ⁻ + H ⁺ + CH ₂ COOH ·
26		CH ₃ COO ⁻ + NO ₃ · = NO ₃ ⁻ + CH ₃ · + CO ₂
27		NO ₃ · + HC ₂ O ₄ ⁻ = NO ₃ ⁻ + H ⁺ + C ₂ O ₄ ⁻
28		NO ₃ · + C ₂ O ₄ ²⁻ = NO ₃ ⁻ + C ₂ O ₄ ⁻
29		NO ₃ · + CH(OH) ₂ CH(OH) ₂ = H ⁺ + NO ₃ ⁻ + CH(OH) ₂ C(OH) ₂ ·
30		NO ₃ · + CH(OH) ₂ COOH = H ⁺ + NO ₃ ⁻ + C(OH) ₂ COOH ·
31		NO ₃ · + Br ⁻ = NO ₃ ⁻ + Br ·
32		CO ₃ ²⁻ + NO ₃ · = NO ₃ ⁻ + CO ₃ ⁻
33		HCO ₃ ⁻ + NO ₃ · = NO ₃ ⁻ + CO ₃ ⁻ + H ⁺
34		NO ₃ · + Cl ⁻ = NO ₃ ⁻ + Cl ·

Table S2. Summary of the selected nitrate formation cases for the modeling analyses.

	Site	Period	Obs. ΔNO_3^- ($\mu\text{g m}^{-3}$)	Ave. NO_2 (ppb)	Ave. O_3 (ppb)	Ave. NH_3 (ppb)
Daytime	Ji'nan	8:00 – 16:00 16 th May 2014	13.1	19.5	38	14.5
		16:00 – 19:00 5 th Sept. 2015	5.9	12.0	80	11.0
		11:00 – 15:00 10 th Sept. 2015	5.4	12.0	76	24.4
	Yucheng	9:00 – 14:00 25 th Jun. 2014	8.0	23.0	32	12.7
		6:00 – 12:00 5 th Jul. 2014	21.9	24.1	6	54.4
		16:00 – 20:00 15 th Jul. 2014	16.1	9.0	74	23.0
	Mt. Tai	11:00 – 16:00 31 st Jul. 2014	11.5	3.1	84	38.9
		8:00 – 17:00 15 th Aug. 2014	9.5	2.0	77	29.4
		15:00 – 20:00 19 th Aug. 2014	13.4	10.6	88	21.5
		8:00 – 15:00 21 st Aug. 2014	5.8	3.2	92	24.2
Nighttime	Ji'nan	19:00 11 st – 0:00 12 nd May 2014	10.6	14.2	13	24.7
		19:00 16 th – 3:00 17 th May 2014	23.8	22.8	35	33.1
		20:00 9 th – 1:00 10 st Sept. 2015	10.9	17.8	21	23.2
	Yucheng	3:00 – 9:00 8 th Jun. 2014	10.1	39.7	19	30.2
		23:00 26 th – 8:00 27 th Jun. 2014	17.1	14.3	18	18.0
		20:00 8 th – 8:00 9 th Jul. 2014	33.8	25.6	13	56.3
		21:00 12 nd – 8:00 13 rd Jul. 2014	21.6	15.7	20	32.1
		21:00 13 rd – 5:00 14 th Jul. 2014	32.7	35.0	24	51.9
	Mt. Tai	19:00 – 23:00 28 st Jul. 2014	11.9	7.1	81	45.1
		21:00 25 th – 3:00 26 th Aug. 2014	10.5	2.3	86	24.4
20:00 26 th – 0:00 27 th Aug. 2014		7.4	5.7	96	21.1	

Table S3. Initial setup of daytime model experiment for nitrate formation

Species	Initial values
SO ₂	10 ppbv
O ₃	60 ppbv
NO ₂	0-200 ppbv
NH ₃	0-40 ppbv
NO ₃ ⁻	0 μg m ⁻³
Temperature	25 °C
RH	80%
Liquid water content	2 μmol m ⁻³
Average particle radius	100 nm

Table S4. Initial setup of nighttime model experiment for nitrate formation

Species	Initial values
SO ₂	10 ppbv
NH ₃	10 ppbv
NO ₂	0-80 ppbv
O ₃	0-80 ppbv
NO ₃ ⁻	0 μg m ⁻³
Temperature	25 °C
RH	80%
Liquid water content	2 μmol m ⁻³
Average particle radius	100 nm