Supplement of Atmos. Chem. Phys., 18, 11261–11275, 2018
https://doi.org/10.5194/acp-18-11261-2018-supplement
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Atmospheric Chemistry and Physics
Open Access

Supplement of

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

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Table S1. The chemical reactions related to nitrate formation in the RACM2/CAPRAM2.4.

No.	Categorized pathways	Reactions	Rate constants ($cm^3\ mol^{-1}\ s^{-1}$)
1		$HNO_3(g) \leftrightarrow HNO_3(a)$	$k_f = 1/(r^2/(3*d_1)+4*r/(3*v_1*\alpha_1))$ $k_b = 1/(r^2/(3*d_1)+4*r/(3*v_1*\alpha_1))/(h_1*R*T)$
2		$HNO_3(a) \leftrightarrow H^+ + NO_3^-$	$k_f = 1.1*10^{12}*e^{(-TCORR*(-1800))}$ $k_b = 5.0*10^{13}$
3	***HNO_3 formation and partitioning***	$NH_3(g) \leftrightarrow NH_3(a)$	$k_f = 1/(r^2/(3*d_2)+4*r/(3*v_2*\alpha_2))$ $k_b = 1/(r^2/(3*d_2)+4*r/(3*v_2*\alpha_2))/(h_2*R*T)$
4		$NH_3(a) + H_2O(a) \leftrightarrow NH_4^+ + OH^-$	$k_f = 6.02*10^8*e^{(-TCORR*560)}$ $k_b = 3.4*10^{13}$
5		$H^+ + OH^- \leftrightarrow H_2O(a)$	$k_f = 1.3*10^{14}$ $k_b = 2.34*10^{-5}*e^{(-TCORR*6800)}$
6		$N_2O_5(g) \leftrightarrow N_2O_5(a)$	$k_f = 1/(r^2/(3*d_3)+4*r/(3*v_3*\alpha_3))$ $k_b = 1/(r^2/(3*d_3)+4*r/(3*v_3*\alpha_3))/(h_3*R*T)$
7	***N_2O_5 hydrolysis***	$N_2O_5(a) + H_2O(a) \rightarrow 2H^+ + 2NO_3^-$	$5.0*10^{12}$
8		$N_2O_5(a) \rightarrow NO_2^+ + NO_3^-$	$1.0*10^9$
9		$NO_2^+ + H_2O(a) \rightarrow NO_3^- + 2H^+$	$8.9*10^{10}$
10		$NO_2^+ + Cl^- \rightarrow ClNO_2(a)$	$1.0*10^{13}$
11		$NO_3\cdot(g) \leftrightarrow NO_3\ (a)$	$k_f = 1/(r^2/(3*d_4)+4*r/(3*v_4*\alpha_4))$ $k_b = 1/(r^2/(3*d_4)+4*r/(3*v_4*\alpha_4))/(h_4*R*T)$
12		$NO_3\ (a) + OH^- \rightarrow NO_3^- + OH\ (a)$	$9.4*10^{10}*e^{(-TCORR*2700)}$
13		$NO_3\ (a) + Fe^{2+} \rightarrow NO_3^- + Fe^{3+}$	$8.0*10^9$
14		$NO_3\ (a) + Mn^{2+} \rightarrow NO_3^- + Mn^{3+}$	$1.1*10^9$
15		$NO_3\ (a) + H_2O_2(a) \rightarrow NO_3^- + H^+ + HO_2\ (a)$	$4.9*10^9*e^{(-TCORR*2000)}$
16		$NO_3\ (a) + CH_3O_2H(a) \rightarrow NO_3^- + H^+ + CH_3O_2\cdot$	$4.9*10^9*e^{(-TCORR*2000)}$
17	***NO_3 radical aqueous-phase reactions***	$NO_3\ (a) + HO_2\cdot \rightarrow NO_3^- + H^+ + O_2\ (a)$	$3.0*10^{12}$
18		$NO_3\ (a) + O_2^- \rightarrow NO_3^- + O_2\ (a)$	$3.0*10^{12}$
19		$NO_3\ (a) + HSO_3^- \rightarrow NO_3^- + H^+ + SO_3^-$	$1.3*10^{12}*e^{(-TCORR*2000)}$
20		$NO_3\ (a) + SO_3^{2-} \rightarrow NO_3^- + SO_3^-$	$3.0*10^{11}$
21		$NO_3\ (a) + HSO_4^- \rightarrow NO_3^- + H^+ + SO_4^-$	$2.6*10^8$
22		$NO_3\ (a) + SO_4^{2-} \rightarrow NO_3^- + SO_4^-$	$1.0*10^8$
23		$NO_2^- + NO_3\cdot(a) \rightarrow NO_3^- + NO_2\ (a)$	$1.4*10^{12}$
24		$OHCH_2SO_3^- + NO_3\cdot(a) \rightarrow NO_3^- + OHCH_2SO_3\ (a)$	$4.2*10^9$
25		$CH_3OH(a) + NO_3\cdot(a) \rightarrow NO_3^- + H^+ + CH_2OH\ (a)$	$5.4*10^8*e^{(-TCORR*4300)}$

26	$CH_3CH_2OH(a) + NO_3\cdot(a) \rightarrow NO_3^- + H^+ + CH_3CHOH\ (a)$	$2.2*10^9*e^{(-TCORR*3300)}$
27	$CH_2(OH)_2(a) + NO_3\cdot(a) \rightarrow NO_3^- + H^+ + CH(OH)_2\ (a)$	$1.0*10^9*e^{(-TCORR*4500)}$
28	$CH_3CH(OH)_2(a) + NO_3\cdot \rightarrow NO_3^- + H^+ + CH_3C(OH)_2\ (a)$	$1.9*10^9$
29	$CH_3CHO(a) + NO_3\cdot(a) \rightarrow NO_3^- + H^+ + CH_3CO\ (a)$	$1.9*10^9$
30	$HCOOH + NO_3\cdot(a) \rightarrow NO_3^- + H^+ + CO_2H\ (a)$	$3.8*10^8*e^{(-TCORR*3400)}$
31	$HCOO^- + NO_3\cdot(a) \rightarrow NO_3^- + CO_2H\ (a)$	$5.1*10^{10}*e^{(-TCORR*2200)}$
32	$CH_3COOH(a) + NO_3\cdot(a) \rightarrow NO_3^- + H^+ + CH_2COOH\ (a)$	$1.4*10^7*e^{(-TCORR*3800)}$
33	$CH_3COO^- + NO_3\cdot(a) \rightarrow NO_3^- + CH_3\ \cdot + CO_2(a)$	$2.9*10^9*e^{(-TCORR*3800)}$
34	$NO_3\ (a) + HC_2O_4^- \rightarrow NO_3^- + H^+ + C_2O_4^-$	$6.8*10^{10}$
35	$NO_3\ (a) + C_2O_4^{2-} \rightarrow NO_3^- + C_2O_4^-$	$2.8*10^{11}$
36	$NO_3\ (a) + CH(OH)_2CH(OH)_2(a) \rightarrow H^+ + NO_3^- + CH(OH)_2C(OH)_2\ (a)$	$1.1*10^9*e^{(-TCORR*3368)}$
37	$NO_3\ (a) + CH(OH)_2COOH(a) \rightarrow H^+ + NO_3^- + C(OH)_2COOH\ (a)$	$1.1*10^9*e^{(-TCORR*3368)}$
38	$NO_3\ (a) + Br^- \rightarrow NO_3^- + Br\ (a)$	$3.8*10^{12}$
39	$CO_3^{2-} + NO_3\cdot(a) \rightarrow NO_3^- + CO_3^-$	$4.1*10^{10}$
40	$HCO_3^- + NO_3\cdot(a) \rightarrow NO_3^- + CO_3^- + H^+$	$4.1*10^{10}$
41	$NO_3\ (a) + Cl^- \rightarrow NO_3^- + Cl\ (a)$	$3.4*10^{11}*e^{(-TCORR*4300)}$

R=82.056. TCORR = (1/T - 1/298). r is the particle radius. d_i is the diffusion coefficient. V_i is the molecular speed of the relevant species. α_i is the accommodation coefficient. h_i is the henry constant.

Table S2. Overview of the field measurements in the present study

Area	Measurement period	Location	Description
Ji'nan	5th-17th May 2014, 23rd Aug. - 21st Sep. 2015	Central Campus of Shandong University (36.67 °N, 117.06 °E, ~50 m a.s.l.)	Urban
Yucheng	2nd Jun. - 16th Jul. 2014	Chinese Academy of Sciences Comprehensive Station (36.87 °N, 116.57 °E, ~23 m a.s.l.)	Rural
Mt. Tai	23rd Jul. - 27th Aug. 2014	North side of Mountain Peak (36.26 °N, 117.11 °E, 1465 m a.s.l.)	Remote

Table S3. Initial concentrations of major VOC compounds for the model simulations (unit: ppbv)

Species	Ji'nan	Yucheng	Mt. Tai	Species	Ji'nan	Yucheng	Mt. Tai
Ethane	2.01	2.66	2.30	Propene	1.88	0.42	0.08
Propane	1.89	1.14	0.82	1-Butene	0.34	0.04	0.02
n-Butane	——	0.51	0.41	cis-2-Butene	1.62	0.03	——
i-Butane	——	0.38	0.32	trans-2-Butene	0.27	——	——
n-Pentane	0.30	0.16	0.13	1-Pentene	0.15	0.01	0.01
n-Hexane	0.27	0.74	0.06	cis-2-Pentene	0.22	——	——
2-Methylpentane	0.27	0.10	0.05	trans-2-Pentene	0.09	——	——
3-Methylpentane	0.32	0.06	0.03	Isoprene	0.18	0.39	0.15
2,2-Dimethylbutane	0.16	0.04	——	α-Pinene	——	——	0.08
2,3-Dimethylbutane	0.20	0.03	0.01	β-Pinene	——	——	0.02
Cyclopentane	2.49	0.03	0.02	Toluene	1.01	0.91	0.24
Cyclohexane	0.53	0.03	0.03	o-Xylene	0.35	0.07	0.03
Methylcyclopentane	0.20	0.05	——	m/p-Xylene	0.55	0.08	0.09
n-Heptane	0.13	0.05	0.02	1,2,3-Trimethylbenzene	0.11	——	0.02
3-Methylhexane	0.20	0.04	——	1,2,4-Trimethylbenzene	0.18	——	0.05
2,3-DimethylPentane	0.20	0.02	——	1,3,5-Trimethylbenzene	0.09	0.10	0.01
Methylcyclohexane	0.09	0.04	——	2-Ethyltoluene	0.1	0.09	0.01
n-Octane	0.16	0.05	0.01	3-Ethyltoluene	0.07	0.09	0.03
2-Methylheptane	0.25	——	——	4-Ethyltoluene	0.12	0.10	0.01
2,2,4-Trimethylpentane	0.08	——	——	Ethylbenzene	0.26	0.09	0.07
n-Nonane	0.12	0.04	0.02	m-Diethylbenzene	0.05	——	——
n-Decane	0.12	0.03	——	p-Diethylbenzene	0.05	——	——
n-Undecane	0.06	0.04	——	n-Propylbenzene	0.08	0.08	0.01
Ethene	1.73	0.90	0.59	Styrene	0.21	0.02	——

These VOC data were taken from the previous studies in urban Ji'nan and at the same sites of Yucheng and Mt. Tai (Wang et al., 2015; Zhu et al., 2016 and 2017). The VOC measurements were made by an online GC/FID analyzer in urban Ji'nan and by offline sampling coupled with GC/FID/MS analyses at Yucheng and Mt. Tai.

Table S4. Summary of the selected nitrate formation cases for the modeling analyses.

Period	Site	Period	Obs. △NO_3^- (μg m^{-3})	Avg. NO_2 (ppb)	Avg. O_3 (ppb)	Avg. NH_3 (ppb)
Daytime	Ji'nan	9:00 – 16:00 16th May 2014	12.5	19.9	40	14.9
		15:00 – 18:00 5th Sept. 2015	7.7	11.2	87	11.0
		11:00 – 14:00 10th Sept. 2015	5.4	12.0	76	24.4
	Yucheng	9:00 – 14:00 25th Jun. 2014	8.0	23.0	32	12.7
		9:00 – 12:00 5th Jul. 2014	15.8	28.7	11	61.6
		16:00 – 19:00 15th Jul. 2014	16.1	9.0	74	23.0
	Mt. Tai	11:00 – 15:00 31st Jul. 2014	11.5	3.1	84	38.9
		8:00 – 16:00 15th Aug. 2014	9.5	2.0	77	29.4
		15:00 – 19:00 19th Aug. 2014	13.4	10.6	88	21.5
		8:00 – 14:00 21st Aug. 2014	5.8	3.2	92	24.2
Nighttime	Ji'nan	19:00 – 23:00 11st May 2014	10.6	14.2	13	24.7
		19:00 16th – 2:00 17th May 2014	23.8	22.8	35	33.1
		20:00 9th – 0:00 10st Sept. 2015	10.9	17.8	21	23.2
	Yucheng	3:00 – 6:00 8th Jun. 2014	5.2	43.5	10	28.6
		23:00 26th – 6:00 27th Jun. 2014	14.5	15.0	17	13.6
		20:00 8th – 6:00 9th Jul. 2014	21.6	26.4	13	53.4
		21:00 12nd – 6:00 13rd Jul. 2014	15.4	15.8	18	25.4
		21:00 13rd – 4:00 14th Jul. 2014	32.7	35.0	24	51.9
	Mt. Tai	19:00 – 22:00 28st Jul. 2014	11.9	7.1	81	45.1
		21:00 25th – 2:00 26th Aug. 2014	10.5	2.3	86	24.4
		20:00 – 23:00 26thAug. 2014	7.4	5.7	96	21.1

Table S5. 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 S6. 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

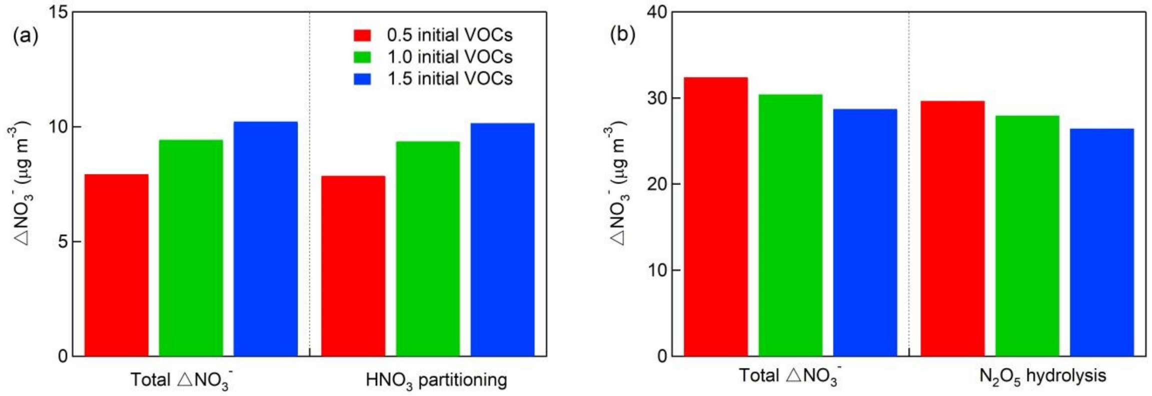

Figure S1. Sensitivity of the model-simulated (a) daytime and (b) nighttime nitrate formation to the initial VOCs

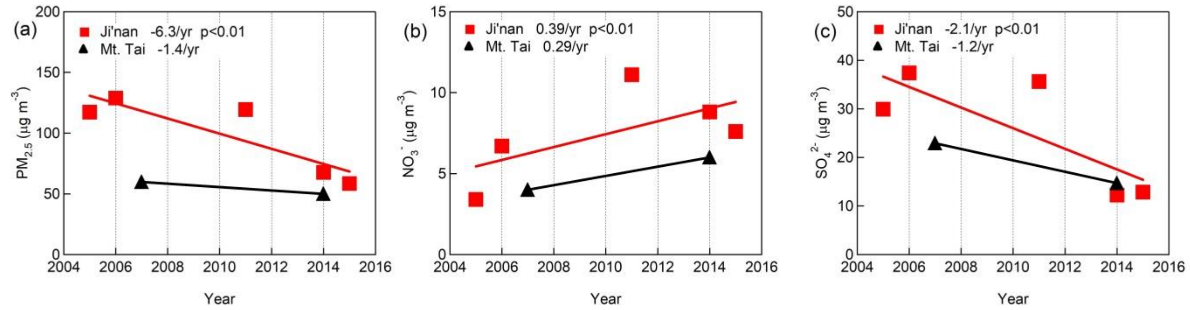

Figure S2. Long-term trends in the absolute concentrations of (a) $PM_{2.5}$, (b) NO_3^-, and (c) SO_4^{2-} in urban Ji’nan and at Mt. Tai in summertime from 2005 to 2015. The fitted lines are derived from the least square linear regression analysis, with the slopes and p values (99% confidence intervals) denoted.

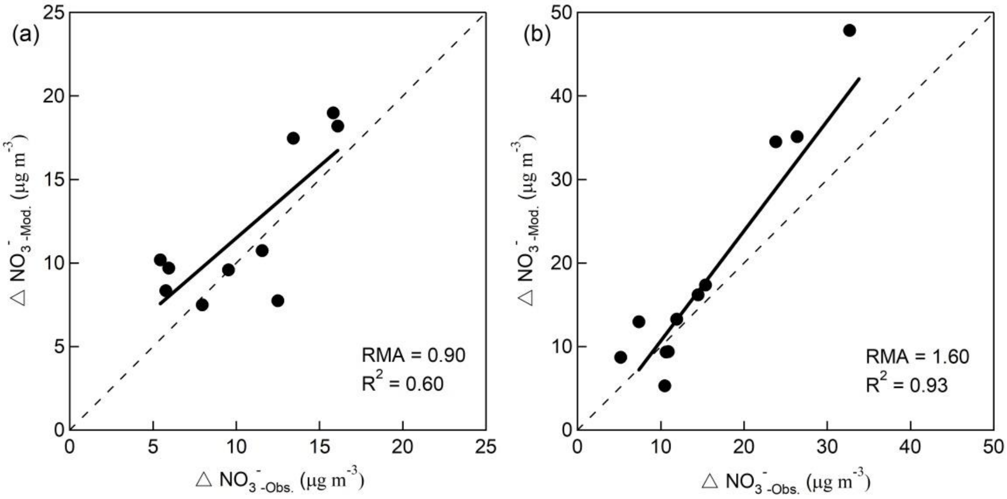

Figure S3. Scatter plots of the modeled versus observed increase of particulate nitrate for the selected daytime (a) and nighttime (b) cases.

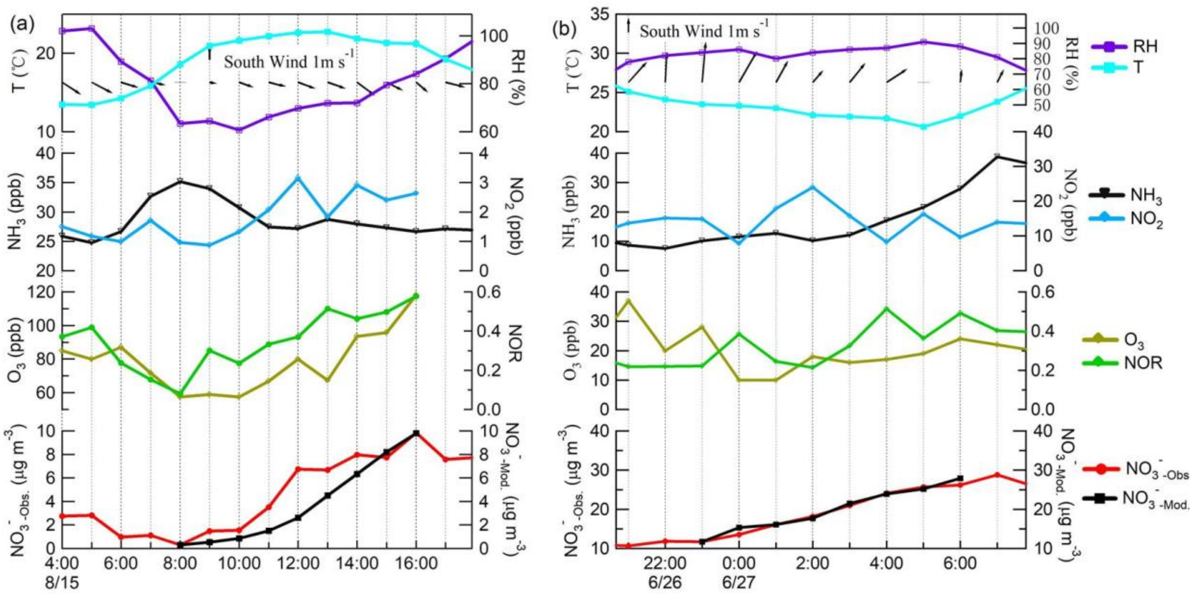

Figure S4. Comparison of the modeled versus observed nitrate concentrations as well as related species for two typical cases at (a) daytime and (b) nighttime.

References:

Wang, N., Li, N., Liu, Z., and Evans, E.: Investigation of chemical reactivity and active components of ambient VOCs in Jinan, China, Air Quality, Atmosphere & Health, 9, 785-793, 2015.

Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L., Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile organic compounds and the influence of biomass burning at a rural site in Northern China during summer 2013, Atmos. Environ., 124, 156-165, 2016.

Zhu, Y., Yang, L., Kawamura, K., Chen, J., Ono, K., Wang, X., Xue, L., and Wang, W.: Contributions and source identification of biogenic and anthropogenic hydrocarbons to secondary organic aerosols at Mt. Tai in 2014, Environ. Pollution, 220, 863-872, 2017.